JUN 2 6 1933

U.S. DEPARTMENT OF COMMERCE

BUREAU OF STANDARDS JOURNAL OF RESEARCH

Vol. 10 MAY 1933 No. 5

CONTENTS

RP. No.	TITLE AND AUTHOR	Page
549.	Screw micrometer gages for rubber specimens. W. L. Holt	575
550.	A resistance-coupled amplifier for measuring ionization currents. L. F. Curtiss	583
551.	"Tin-free" leaded bearing bronze. H. K. Herschman and J. L. Basil	591
552.	Purification of hydrocarbons by crystallization from liquid methane. Isolation of 2-methylheptane from petroleum. R. T. Leslie	609
553.	The effect of altitude on the limits of safe operation of gas appliances. John H. Eiseman, Francis A. Smith, and Cecil J. Merritt	619
554.	Isolation of ethylbenzene from an Oklahoma petroleum. Joseph D. White and F. W. Rose, Jr.	639
555.	The flexometer, an instrument for evaluating the flexural properties of cloth and similar materials. Herbert F. Schiefer	647
556.	A method of exciting resonant vibrations in mechanical systems. L. B. Tuckerman, H. L. Dryden, and H. B. Brooks	659
557.	Conditions affecting the freezing temperature of silver. Wm. F. Roeser and A. I. Dahl	661
558.	Long-wave arc spectra of alkalis and alkaline earths. William F. Meggers	669
559.	The determination of stresses from strains on three intersecting gage lines and its application to actual tests. Wm. R. Osgood and Rolland G. Sturm	685
560.	Critical solution temperatures of mixtures of gasoline, ethyl alcohol, and water. Oscar C. Bridgeman and Dale W. Querfeld	693

BUREAU OF STANDARDS JOURNAL OF RESEARCH

CONTENTS OF RECENT NUMBERS

November 1932 (Vol. 9, No. 5)

RP493. The variation with angle of emission of the radiation from metals bombarded by slow electrons. C. Boeckner. Price 5 cents.

RP494. Nitrogen content of some standard sample steels. J. G. Thompson and E. H. Hamilton. Price 5 cents.

RP495. Analytical methods for the determination of levulose in crude products. R. F. Jackson, J. A. Mathews, and W. D. Chase. Price 5 cents.

RP496. Determination of alumina and silica in steel by the hydrochloric acid residue method. J. G. Thompson and J. S. Acken. Price 5 cents.

RP497. An analysis of lanthanum spectra La I, La II, La III. Henry Norris Russell and William F. Meggers. Price 10 cents.

RP498. Analysis of weighted silk. Ralph T. Mease. Price 5 cents.

RP499. The heat of formation of hydrgen chloride and some related thermo-dynamic data. Frederick D. Rossini. Price 5 cents.

RP500. Thermal expansion of lead. Peter Hidnert and W. T. Sweeney. Price 5 cents.

December 1932 (Vol. 9, No. 6)

RP501. Isolation of the three xylenes from an Oklahoma petroleum. Joseph D. White and F. W. Rose, Jr. Price 5 cents.

RP502. Characteristic equations of vacuum and gas-filled tungsten-filament lamps. L. E. Barbrow and J. Franklin Meyer. Price 5 cents.

RP503. The calorimetric determination of the intrinsic energy of gases as a function of the pressure. Data on oxygen and its mixtures with carbon dioxide to 40 atmospheres, at 28° C. Frederick D. Rossini and Mikkel Frandsen. Price 5 cents.

RP504. Shear tests of reinforced brick masonry beams. D. E. Parsons, A. H. Stang, and J. W. McBurney. Price 5 cents.

RP505. The measurement of low-voltage X-ray intensities. Lauriston S. Taylor and C. F. Stoneburner. Price 5 cents.

RP506. A multi-range potentiometer and its application to the measurement of small temperature differences. H. B. Brooks and A. W. Spinks. Price 5 cents.

RP507. The density of some soda-lime-silica glasses as a function of the composition. F. W. Glaze, J. C. Young, and A. N. Finn. Price 5 cents.

RP508. Coiled-filament resistance thermometers. C. H. Meyers. Price 5 cents.

RP509. Deflection of cosmic rays by a magnetic field. L. F. Curtiss. Price 5 cents.

RP510. The system: CaO-B_2O_3. Elmer T. Carlson. Price 5 cents.

RP511. A metal-connected glass electrode. M. R. Thompson. Price 5 cents.

January 1933 (Vol. 10, No. 1)

RP512. White-metal bearing alloys: Mechanical properties at different temperatures and service tests. Harry K. Hershman and John L. Basil. Price 5 cents.

RP513. The cause and elimination of night effects in radio range-beacon reception. H. Diamond. Price 10 cents.

RP514. The heat capacity, heat of sublimation, and heat of solution of phosphorus pentoxide. Mikkel Frandsen. Price 5 cents.

RP515. The interference method of measuring thermal expansion. George E. Merritt. Price 5 cents.

RP516. Effect of lathe cutting conditions on the hardness of carbon and alloy steels. T. G. Digges. Price 5 cents.

RP517. Measurements of ultra-violet solar radiation in various localities. W. W. Coblentz, R. Stair, and J. M. Hogue. Price 5 cents.

RP518. Effect of service temperature conditions on the electromotive force of unsaturated portable standard cells. J. H. Park. Price 5 cents.

RP519. The Thomas recording gas calorimeter. R. S. Jessup. Price 5 cents.

RP520. Compressive strength of steel columns incased in brick walls. Albert I. Harris, A. H. Stang, and J. W. McBurney. Price 5 cents.

RP521. Further description and analysis of the first spectrum of xenon. C. J. Humphreys and W. F. Meggers. Price 5 cents.

Research papers, where price is given, are already available, and others will be available in the near future as separates for purchase from the Superintendent of Documents, United States Government Printing Office, Washington, D.C.

U.S. DEPARTMENT OF COMMERCE
DANIEL C. ROPER, Secretary
BUREAU OF STANDARDS
LYMAN J. BRIGGS, Acting Director

BUREAU OF STANDARDS JOURNAL OF RESEARCH

May 1933
Vol. 10, No. 5

UNITED STATES
GOVERNMENT PRINTING OFFICE
WASHINGTON : 1933

For sale by the Superintendent of Documents, Washington, D.C. - - Price 25 cents; $2.50 per year on subscription

For a partial list of previous research papers appearing in BUREAU OF STANDARDS JOURNAL OF RESEARCH see pages 2 and 3 of the cover

RP549

SCREW MICROMETER GAGES FOR RUBBER SPECIMENS

By W. L. Holt

ABSTRACT

Screw micrometers combined with an electrical contact indicating device have been adapted to measuring the dimensions of soft rubber parts. Three types of gages have been built. Two of these are vertical gages for thickness measurements and the other is a horizontal gage for dimensions, such as the width of test specimens and the diameter of cylindrical or spherical parts. Measurements made with the micrometer gages are compared with (1) the thickness or diameter computed from the volume and (2) those made with the usual type of dial gages. The micrometer gage measurements agree very closely with the computed values due to the precision of the micrometer screw and the fact that there is little compression of the rubber at points of contact.

CONTENTS

	Page
I. Introduction	575
II. Indentation of rubber by spherical contacts	575
III. Description of gages	576
IV. Use of gages and precision of measurements	580
V. Comparisons with other methods of measurement	581
VI. Summary	582

I. INTRODUCTION

The screw micrometer as a means of making precise measurements has advantages over many other types of measuring devices, due to simplicity of construction and the fact that it is inherently a high-precision instrument. In adapting it to measuring the dimensions of soft rubber specimens, however, the difficulty arises as to how to determine the point at which the spindle and anvil are in contact with the specimen or the amount of pressure that is being applied to the specimen. The compression of the material due to the applied pressure introduces an error in measurement which may or may not be significant.

In the present work, screw micrometers have been adapted to measurement of rubber parts by the use of electrical contacts, together with an indicating device as a means of determining when the gage foot touches the rubber specimen.

II. INDENTATION OF RUBBER BY SPHERICAL CONTACTS

Theoretically the thickness of a rubber sample is taken to be the distance between the spindle and the foot of the micrometer when each is just touching the sample. In the gages described the aim has been

to use pressures as near zero as possible so that any compression of the sample at the contact with gage parts will be neglible. It is necessary, or at least convenient, to make one of the surfaces of the gage contacts spherical and the other plane, and accordingly, it is desirable to determine the indentations which spherical contacts produce for given loads. To obtain these data, a lever arrangement was used as shown in figure 1. Three lenses having radii of curvature of 0.7 inch, 1 inch, and 2 inches, respectively, were used for the spherical surfaces and two types of rubber—a pure gum and a tread stock were tested. The samples were of sufficient thickness so that the thickness did not influence the amount of indentation. Micrometer readings were taken at a series of loads between 0.02 and 2 g. The measured thickness obtained with each lens was plotted against load for each rubber specimen. Each curve was extended back to the zero load axis to determine the micrometer reading at zero load. Using the micrometer readings at zero load, the actual indentations are readily determined. They are shown graphically in figure 2.

Differences in indentation with the three lenses are small so that they can not be determined with precision by the method used.

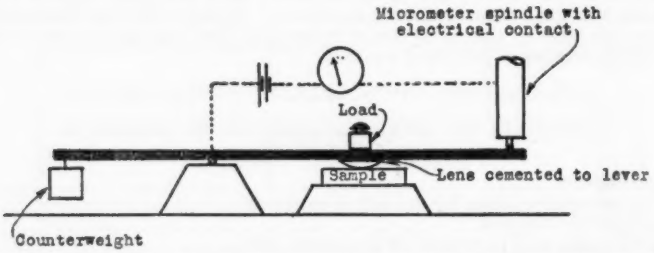


FIGURE 1.—*Line drawing showing lever arrangement used for measuring indentation*

As a whole, however, indentations are found under loads of 1 g (the load subsequently chosen) from 0.0003 to 0.0005 inch for pure gum and from 0.0002 to 0.0003 inch for tread stock. These figures represent indentation errors which may occur under the most unfavorable conditions, but it will be evident from the data presented that the errors enter in different degrees depending upon the dimensions and type of sample measured and the gage used. Based on these indentation data, a radius of curvature of 1 inch was chosen for the spherical contact with a force of not more than 1 g to act upon it. The diameters of contacts in all cases were made sufficiently large so that in the softest rubber the diameter of the contact surface would be less than the diameter of the contact.

III. DESCRIPTION OF GAGES

Three types of gages were developed. Two of these are of the vertical type for making thickness measurements and the third, a horizontal gage for measuring diameters, widths, etc.

Figure 3 illustrates the single contact thickness gage. It consists essentially of a table with an arm spanning it and carrying at its center a standard micrometer head having a ¼-inch spindle. A presser foot with an electrical contact and adjusting screw is mounted on the under side of the table—the foot extending through the table

and free to project about three one-thousandths of an inch above it. The contact surface of the presser foot is a portion of a sphere of 1 inch radius and is mounted at the end of a light spring. When it is pressed down until flush with table top an electrical contact is made which is indicated on the galvanometer. To accomplish this, a force slightly less than 1 g is required. The micrometer is mounted so that it reads zero when the spindle presses down the presser foot and causes electrical contact. Small adjustments which may be necessary due to temperature changes or other causes can be made by moving the index wheel on the spindle or by changing the position of the index guide.

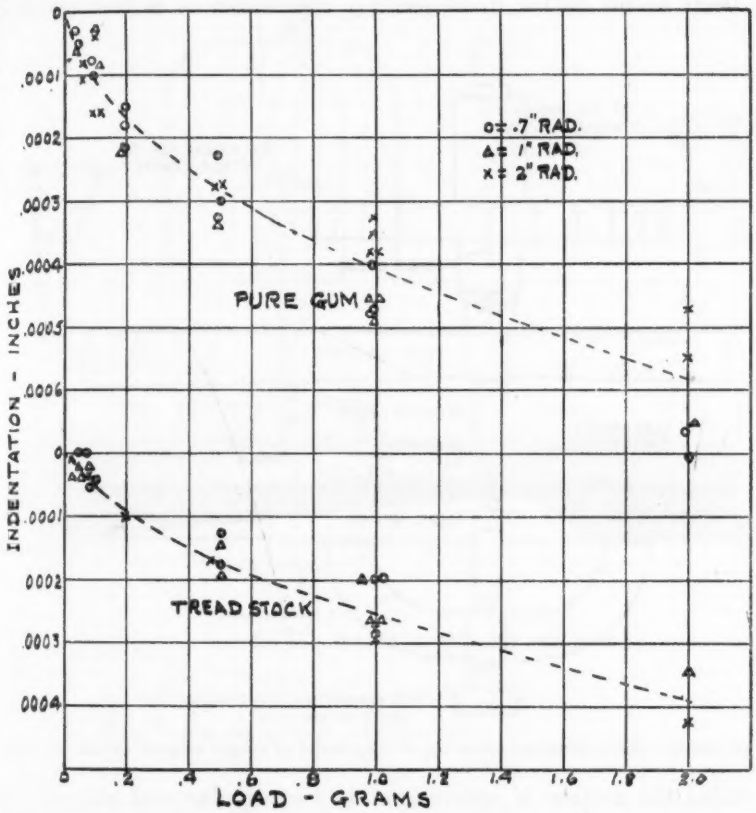


FIGURE 2.—*Indentation of spherical surfaces in pure gum rubber and in tread stock.*

Data are shown for lenses of 0.7 inch, 1 inch, and 2 inches radii, respectively.

Figure 4 illustrates the double contact thickness gage. The general construction is similar to the single contact gage except that a micrometer replaces the lower adjusting screw and electrical contacts and a spherical presser foot are added to the upper micrometer. The lower presser foot is the same as in the single contact gage while the upper one consists of an aluminum rod which is free to move vertically. Its weight is about 0.7 g. Electrical contact is made by movement of the top of this rod which lifts a contact set in a narrow strip of copper foil.

The thickness gages will accommodate specimens up to 1 inch thick.

Figure 5 illustrates the gage used for horizontal measurements. This operates on the same principle as the other gages. The main difference is in the table on which the specimen rests. This table is adjustable in height to permit alignment of the specimen with the micrometer. It has also been found better to adjust the presser foot to project about five one-thousandths of an inch at the time of electrical contact, rather than flush with the carrying arm. The table is slightly inclined so that specimens tend to roll or slip toward the flat micrometer spindle rather than toward the presser foot. The gage has been found useful in measuring the width of a test specimen

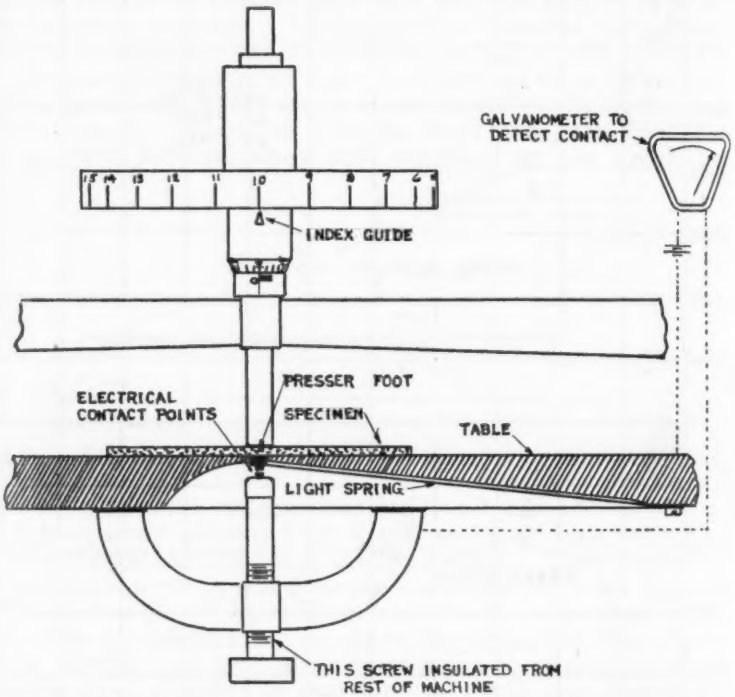


FIGURE 3.—*Line drawing showing arrangement of single contact thickness gage.*

provided the section is approximately rectangular and not too thin. Measurements obviously cannot be depended upon where the cut surfaces are not plane and parallel. When the gage is used for width measurements, a small steel block 0.3 inch long is used, which slides in the central goove. Two positions for the arm carrying the contact foot permit measurements either between zero and 1 inch or between 1 and 2 inches.

In making measurements with any of the gages the specimen is placed between the micrometer spindle and the presser foot (or between the presser feet) and the head or heads turned until contact is made. There is no appreciable difference in measurements whether the "make" or "break" in the circuit is used, but the "make" seems the most convenient. With the double contact gage the difference

between the two micrometer readings is the desired thickness while with the other gages the thickness is read directly. The index wheels permit convenient reading to 0.0001 inch.

The electrical contact points in all the gages are of platinum and the circuits such that the current is extremely small to insure perma-

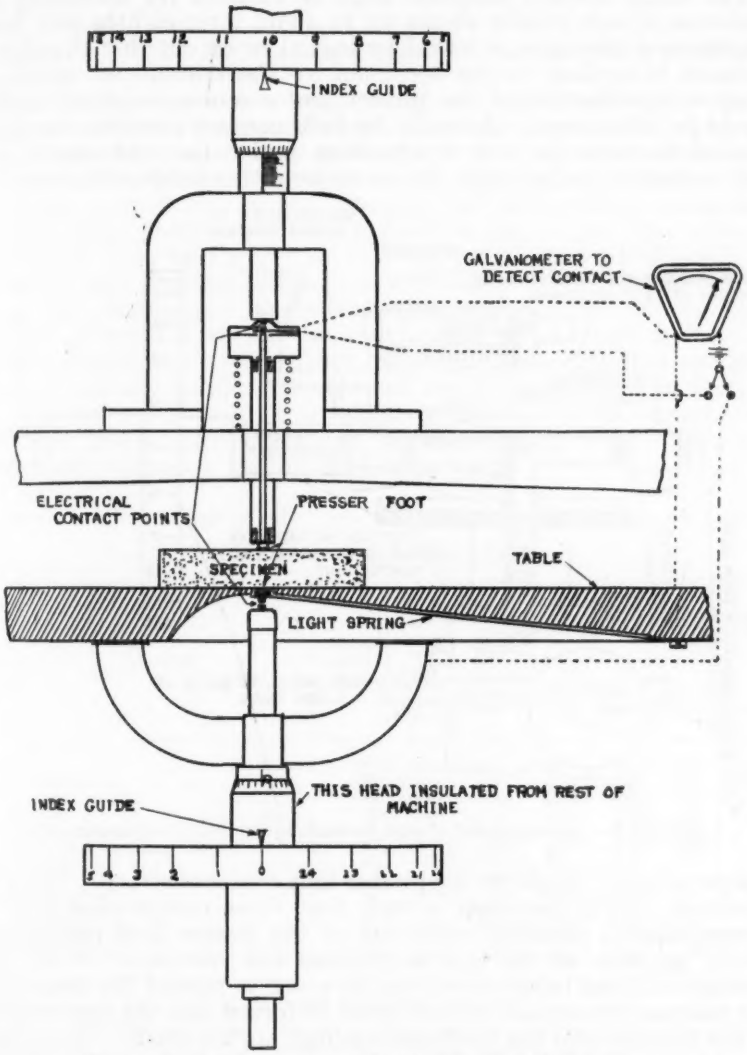


FIGURE 4.—*Arrangement of double contact thickness gage.*

nent contact points. In our work, one dry cell is used with a resistance of 5000 ohms in the circuit and detection made with a sensitive millivoltmeter. The most practical instrument would be a low potential, low current, rugged null point galvanometer, together with a suitable resistance. In using the gages it is convenient to have the galvanometer mounted behind the gage table and 5 or 6 inches

above it. The operator can then read the micrometer and at the same time observe movement of the galvanometer pointer.

IV. USE OF GAGES AND PRECISION OF MEASUREMENTS

The single contact thickness gage is adapted for measuring the thickness of soft rubber sheets up to about three-eighths inch thick. When using this gage it would be logical to expect that if sufficient pressure is applied to the specimen by the micrometer spindle to produce a retraction of the presser foot a serious indentation error would be introduced. Actually for light contact pressures the thickness of material in pure compression under the micrometer contact surface is limited, and the same condition holds with regard to

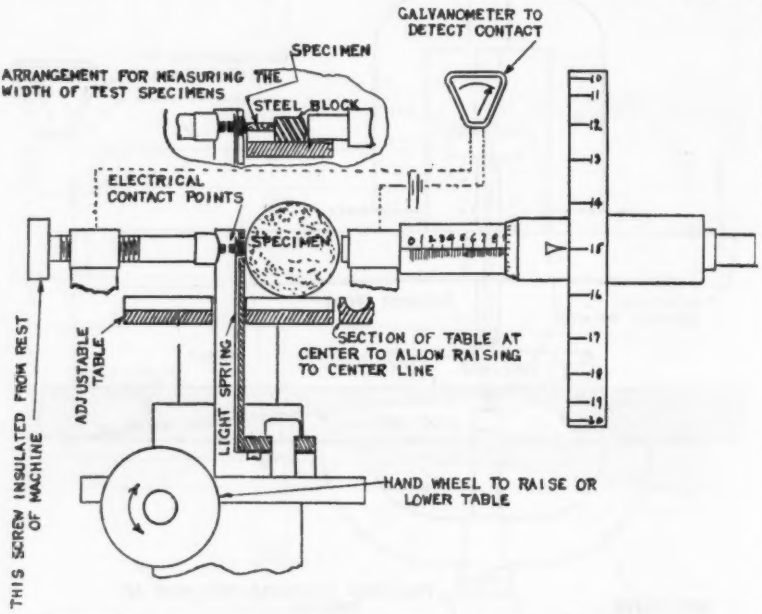

GALVANOMETER TO DETECT CONTACT
SPECIMEN
ARRANGEMENT FOR MEASURING THE WIDTH OF TEST SPECIMENS
STEEL BLOCK
ELECTRICAL CONTACT POINTS
SPECIMEN
ADJUSTABLE TABLE
LIGHT SPRING
SECTION OF TABLE AT CENTER TO ALLOW RAISING TO CENTER LINE
HAND WHEEL TO RAISE OR LOWER TABLE
THIS SCREW INSULATED FROM REST OF MACHINE

FIGURE 5.—*Arrangement of gage for making horizontal measurements.*

a layer of material above the presser foot contact surface. When the thickness of the specimen is such that these compression zones or layers interact directly, retraction of the presser foot results practically as soon as the spindle touches the specimen. With thick specimens it can be observed that in order to retract the presser foot the micrometer contact surface must be forced into the upper surface of the material and the thickness readings are too small. Accordingly for thick materials the double contact gage should be used. In practice it is found that very soft rubber sheets up to three-eighths inch thick can be measured with the single contact gage, although errors due to indentation of the micrometer spindle begin to become apparent at this thickness. The accuracy of measurement with the single contact gage within the ¼-inch range is about 0.0002 inch. At three-eighths inch the accuracy is slightly less. With the double contact gage, which employs two spherical contact surfaces instead of a spherical and a flat surface, indentation errors such as are shown by

figure 2 become evident and measurement of soft stocks may be as much as 0.0008 inch in error due to the two presser feet.

With the horizontal gage, indentation errors due to the one presser foot may amount to 0.0004 inch in soft stocks. Data given later indicate measurements of the diameter of soft rubber rods within this limit.

V. COMPARISON WITH OTHER METHODS OF TESTING

Table 1 shows measurements made with the micrometer gages compared with (1) those made with the usual type of dial gages and (2) thicknesses or diameters computed from volumes. The latter dimensions for rectangular sheets were obtained as follows: Test specimens from 4 to 6 inches square of different rubber compounds and of various thicknesses were molded or cut. Care was taken to make them with true edges so that the length and width could be measured with a precision of about 0.002 inch. The volume of each sheet was determined by hydrostatic weighings and the average thickness computed as the quotient of the volume and area. The average diameters of two rubber rods were also computed similarly from volume and length. Because of the high coefficient of thermal expansion of rubber, care was taken to make all volume determinations and linear measurements at the same temperature. This was particularly necessary for the thick samples.

TABLE 1.—*Dimensions of rubber test specimens determined in different ways*

THICKNESS OF RUBBER SHEETS

Specimen No.	Material	"Shore" hardness	Average thickness computed from volume	Measurements by micrometer gage [1]			Measurements by dial gage [2]	
				Minimum	Average	Maximum	3-ounce weight	9-ounce weight
			Inch	*Inch*	*Inch*	*Inch*	*Inch*	*Inch*
1	Pure gum	45	0.0190	0.0186	0.0190	0.0194	0.019	0.0185
2	do	45	.0760	.0756	.0757	.0761	.0745	.0735
3	do	45	.1328	.1324	.1326	.1328	.131	.128
[3]				.1316	.1320	.1322		
4	Pure gum	45	.2474	.2440	.2474	.2515	.2455	.2435
5	do	45	.3759	.3735	.3755	.3775	.374	.3695
[3] 5				.3730	.3752	.3777		
6	High rubber	48	.0504	.0500	.0508	.0516	.050	.049
7	do	48	.0718	.0707	.0722	.0739	.072	.070
8	Tread stock	70	.0229	.0221	.0231	.0242	.023	.023
9	do	70	.0660	.0643	.0659	.0679	.0655	.065
10	Sheet packing	68	.1221	.1215	.1223	.1228	.122	.1215

DIAMETER OF RUBBER RODS [4]

11	Pure gum	45	.6102	.6078	.6101	.6128		
12	do	45	.9792	.9764	.9788	.9831		

[1] Minimum, maximum, and average of at least 16 measurements.
[2] Average measurements at the same points (corrected by calibration).
[3] Measured with double contact gage.
[4] Minimum, maximum, and average of 18 measurements.

Measurements with each gage were made at the same 16 or more points distributed over a sample and the results averaged. The dial gage used was of standard design graduated to read to 0.001 inch.

In each measurement the ten-thousandths place was estimated. A complete calibration was then made of the dial gage and a correction made for each measurement. These corrections were erratic throughout the range of the instrument, varying from +0.0002 to −0.0006 inch. Average measurements are recorded in the table to the nearest 0.0005 inch.

Specimens nos. 1 to 5 are a series of pure gum sheets of increasing thicknesses and represent the most difficult type of rubber to measure without compression. Up to sample no. 5 the measured thicknesses of samples using the single contact gage do not differ from the computed values by more than 0.0003 inch. No. 5, which is three-eighths inch thick, begins to show the effect of compression of the spindle and indicates the practical limit of use for a gage of this design. Measurements of specimens 3 and 5 made with the double contact gage are shown for comparison. Although the latter specimen can apparently be measured quite satisfactorily with either gage, it is found that the single contact gage is apt to give erroneous results if this limit is exceeded. The thinnest specimen (no. 1) shows very little indication of compression with any gage—all measured thicknesses being practically the same as the computed value. The thicker specimens all show decreases in indicated thickness as one goes from the micrometer gage to the 3-ounce dial reading and to the 9-ounce dial reading.

One would expect the micrometer gage thicknesses to be equal to or slightly less than the computed values, which condition appears to exist for the specimens most uniform in thickness. The fact that the gage measurements are slightly greater than the computed values in some cases is attributed to slight irregularities in the thickness or in the surface of the specimens which tend to make the measured distance high.

With the soft rubber rods, specimens 11 and 12, the measured diameters are within 0.0001 and 0.0004 inch, respectively, of the computed values. No suitable dial gage was available for measuring the diameters.

VI. SUMMARY

The micrometer gages described are adapted to measuring samples covering a wide range of sizes and shapes. These include the thickness of sheets up to 1 inch, the width of test specimens, and the diameters of rods and spheres up to 2 inches.

The gages eliminate or reduce errors due to compression of the rubber at points of contact, and for this reason are particularly adapted to soft compounds.

The advantage of the micrometer gages lies in accuracy of measurement due to the design of gages and the inherent precision of the micrometer screw.

WASHINGTON, February 16, 1933.

A RESISTANCE-COUPLED AMPLIFIER FOR MEASURING IONIZATION CURRENTS

By L. F. Curtiss

ABSTRACT

A description is given of a simple two-stage resistance-coupled vacuum-tube amplifier for use in measuring ionization currents down to the order of 10^{-13} ampere. Commercial dry-cell vacuum tubes are used. It can be calibrated and will retain its calibration over considerable periods within 1 percent. Where comparative measurements are required—for example, standardizing radium preparations—it is capable of a much higher accuracy. Readings are made on a pointer-type microammeter. The stability of the circuit indicates that a more sensitive instrument could be used if more feeble currents are to be measured. A description of interchangeable ionization chambers, suitable for use with such an amplifier, is given.

CONTENTS

		Page
I.	Introduction	583
II.	Description of the amplifier	584
III.	Mounting for ionization chambers	585
IV.	Calibration of amplifier	587
V.	Ionization chambers	588
VI.	Acknowledgments	589

I. INTRODUCTION

Many devices have been developed to make use of the amplifying properties of vacuum tubes for the measurement of ionization currents. These vary in sensitivity from circuits using the FP-54 tube,[1] capable of detecting currents of the order of 10^{-17} ampere to more insensitive arrangements intended for the measurement of heavier currents. Unfortunately such devices have not come into general use for measuring ionization currents produced by the radiations from radioactive substances. An important obstacle in the adoption of vacuum-tube amplifiers for the measurement of such currents, which range approximately from 10^{-10} to 10^{-14} amperes, has been the lack of suitable resistors for use in the input stage. Recently very satisfactory resistors of the order of 10^{10} ohms have been made available commercially. This paper is intended to call attention to the great improvement in methods of measuring ionization currents which have thus been made available.

An amplifier, to be used advantageously for such purposes, must possess the following features: (1) direct instantaneous readings, eliminating timing of moving indicators by a stop watch or other timing device; (2) rugged, dead-beat indicating instrument, such as

[1] Dubridge, L. A., Phys. Rev., vol. 37, p. 392, 1931.

microammeter or galvanometer of moderate sensitivity; (3) considerable range of sensitivity; and (4) reasonable accuracy in reproduction of readings from day to day. The writer has investigated the possibility of constructing such an amplifier and has found that a very simple two-stage resistance-coupled amplifier will accomplish the purpose. Such an arrangement can be made to give a current amplification of about 10^6 without appreciable unsteadiness in the indicating instrument. An amplifier of this type has been used for α-ray and β-ray measurements in the radium laboratory of the Bureau of Standards for about a year, and has met all ordinary requirements with a considerable saving in time. A description of the amplifier and some forms of ionization chambers which may be used with it is given in this paper.

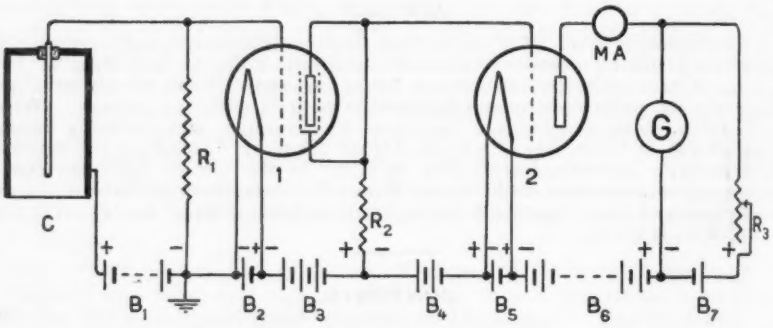


FIGURE 1.—*Wiring diagram of amplifier.*

C=ionization chamber.
B_1=1,000 volts, B_2=2 volts, B_3=6 volts, B_4=3 volts.
B_5=2 volts, B_6=90 volts, B_7= 1.5 volts.
R_1=10^{10} ohms, R_2=0.5 megohm, R_3=6-ohm and 1,000 ohm rheostats in series.
MA=milliammeter.
G=microammeter.
No. 1='32 vacuum tube. No. 2='30 vacuum tube.

II. DESCRIPTION OF THE AMPLIFIER

Although the amplifier is of the ordinary direct-resistance-coupled type, it has been found that any marked departure from the arrangement finally adopted leads to trouble, so that a reasonably detailed description of the complete circuit is given. The chief source of difficulty seems to arise from ionization and creeping of electric charges in the first tube of the amplifier. Ionization of the residual gas in this tube can be avoided by keeping the plate voltage below about 6 volts, and the creeping of charges is also partially avoided by this precaution. The effect of this creeping can be eliminated sufficiently for all practical purposes by turning on the amplifier 2 or 3 hours before using it.

The amplifier consists of two stages, as shown in figure 1. A '32 type of radio tube is used in the first stage, *1*, and a '30 type in the second stage, *2*. These tubes are selected because they can be operated very conveniently and economically from dry cells which can be completely screened to reduce disturbances from outside. The screen-grid tube is used in the first stage since it has a control-grid lead brought out at the top which affords better insulation of the grid than is available in those tubes which have the control grid brought out

at the base. The screen grid and plate of this tube are connected together.

The choice of voltages and resistors is fairly important for satisfactory operation, and those used by the writer are given in detail in the legend. C represents the ionization chamber, the collecting rod of which is connected directly to the control grid of the first tube. B_1 is the battery which supplies a saturation voltage for the chamber. For complete steadiness it was found necessary to add a high resistance, R_1, across the input of the first stage. B_2 is the filament battery for the first tube. When using dry cells for this purpose, a rheostat and voltmeter for maintaining the proper filament voltage are desirable, although the sensitivity of the amplifier does not depend greatly on the filament temperature. B_3 supplies the plate potential for the first tube, and R_2 is the coupling resistor between the two stages. B_4 provides the negative bias for the second stage. B_5 is the filament battery for the second tube. Since this battery is about 10 or 12 volts above ground potential, it must be insulated to prevent short circuits. B_6 is the plate battery for the second tube and B_7 is a balancing battery for the circuit containing the meter G, used for actual measurements. The millimeter, MA, is used to indicate the plate current of the second tube and serves to show whether the amplifier is in operation.

Measurements of ionization currents are made by means of the meter G, which may be a pointer type microammeter, in connection with the battery B_7 and the rheostat R_3. The operation consists in adjusting the rheostat R_3 until the reading of the meter G is zero when the chamber C is exposed to no ionizing agent. This meter will then indicate a current proportional to the current flowing in the ionization chamber when exposed to ionizing radiation.

For the most satisfactory operation all parts of the circuit should be electrostatically shielded. In addition, all connections to the grid of the first tube must be screened from the radiation to be measured. This presents some difficulty when, as frequently occurs, γ-radiation is to be measured. Since it is desirable to make the connection between the ionization chamber and grid as short as possible to avoid increasing the electrostatic capacity of the system, it is not convenient to screen this connection from radiation. The problem can be solved by nullifying the effect of the ionization produced between this connection and its grounded shield. This can be done by filling this space with a solid insulating material, such as hard rubber or ceresin. Since this connection is grounded through the resistance R_1, of the order of 10^{10} ohms, a high degree of insulation is not required.

III. MOUNTING FOR IONIZATION CHAMBERS

The use of a screen grid tube makes it easy to provide a way of attaching ionization chambers to the amplifier so that the disturbance due to ionization around the grid lead is eliminated and also makes possible an arrangement so that different forms of ionization chambers can be substituted conveniently for the one in use at the moment. This greatly extends the usefulness of the equipment, since the same apparatus may be used to serve the purpose of an α-ray, β-ray, or γ-ray electroscope by attaching the proper kind of ionization chamber.

The method of mounting the tube and ionization chamber is shown in figure 2. As is shown, the screen grid tube is mounted in an inverted position, a short connection running down a shielded stem

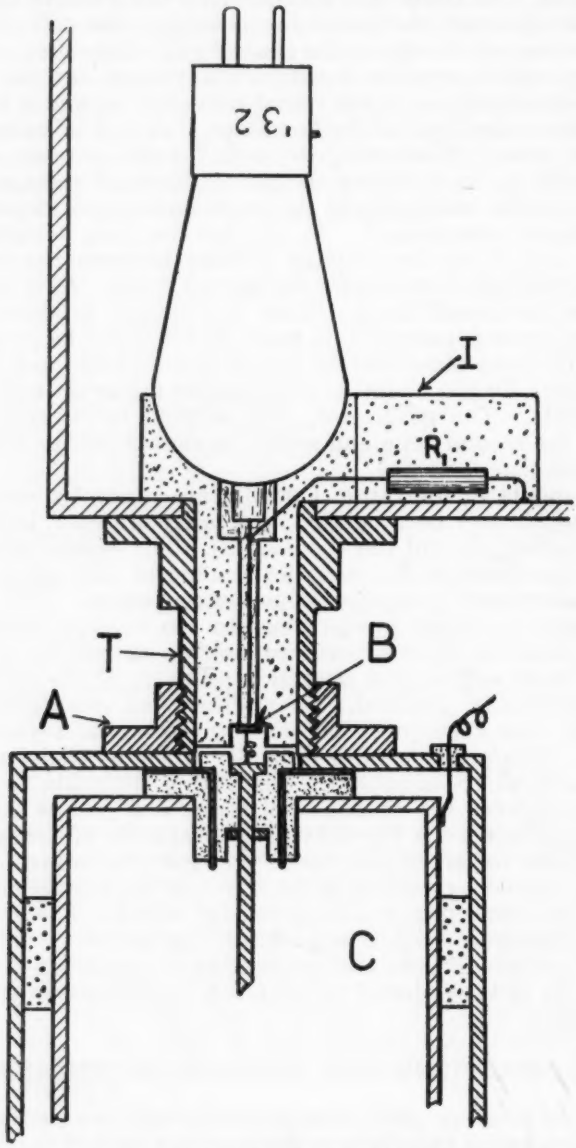


FIGURE 2.—*Mounting for ionization chamber.*

T=connecting stem, *B*=control button, *A*=threaded collar, *C*=ionization chamber, $R_1=10^{16}$ ohms *I*=solid insulation.

to make connection with the ionization chamber *C* below. This connection terminates in a metal button, *B*. The ionization chamber is supported by a threaded collar, *A*, which fits the threaded portion

of the tube T, and when screwed into position a short spiral spring attached to the collector of the ionization chamber is pressed against this button, completing the connection. This permits the ready removal of the ionization chamber. The resistor R_1 is also embedded in the solid insulation I, to protect it from ionization.

IV. CALIBRATION OF AMPLIFIER

The amplifier was calibrated indirectly by attaching an ionization chamber made according to the dimensions given by Irene Curie.[2] Using this chamber, Curie states that one millicurie of radon in a thin-walled α-ray bulb produces an ionization current of 0.064 e.s.u. when placed at 40 cm from the aluminum window. With this ionization chamber connected to the amplifier a deflection of approximately 10 microamperes per millicurie of radon was obtained at a distance of 40 cm. Hence the amplifier yields a deflection of 1 microampere for an ionization current of about 2×10^{-12} amperes under the conditions described. By using a more sensitive instrument in place of the microammeter—for example, a galvanometer with a sensitivity of the order 10^{-9} amperes per millimeter—it is possible to measure currents down to 10^{-14} amperes.

The calibration of the amplifier was made after it had been in continuous operation for about 4 hours. This was necessary because it was found that a slow decrease in sensitivity of the amplifier occurs during the first 2 hours of operation. This decrease is attributed to a slow accumulation of charge on the inner walls of the vacuum tubes which finally attains a saturation value. Careful tests have been made with the amplifier in continuous operation for periods up to 48 hours and no change in the sensitivity occurs after about 3 hours. Readings taken over these periods agreed with each other within 1 percent.

For purposes of checking the calibration conveniently over longer periods, a comparison was made between a thin-walled radon bulb and a radium standard. The radium preparation was exposed to the chamber without screening. The radiation was thus subjected only to the absorption occurring in the glass wall of the containing tube and in the salt of the preparation itself. For the radium preparation used for this comparison with an α-ray bulb filled with radon, it was found that 1 mc of radon was equivalent to 1.85 mg of radium. Although this ratio depends upon the thickness of the aluminum window of the ionization chamber, the thickness of the glass walls of the tube containing the radium, and the distribution of salt in the radium preparation, as well as the wall thickness of the radon bulb, for conditions approximating those described here it gives roughly the amount of absorption of β-radiation to be expected in the salt and container for a radium preparation sealed in glass. The rapidity with which measurements may be made with this arrangement reduces the possibility of errors arising from fluctuations of temperature and barometric pressure. It also makes it very suitable for measurement of radiation from radioactive products of rapid decay, since continuous observation of the intensity of the radiation is possible.

[2] Curie, I., J. de Phys., vol. 22, p. 472, 1925.

V. IONIZATION CHAMBERS

To indicate the variety of uses to which the amplifier may be put by means of interchangeable ionization chambers, four principal types of chambers are sketched in figure 3. These chambers are all fitted with a threaded collar, *A*, by which they may be attached to the amplifier. This collar is fastened to the outside grounded case which provides the electrical shielding for the chamber.

An α-ray chamber is shown at *a*, constructed so that the active material may be introduced directly into the interior. The bottom

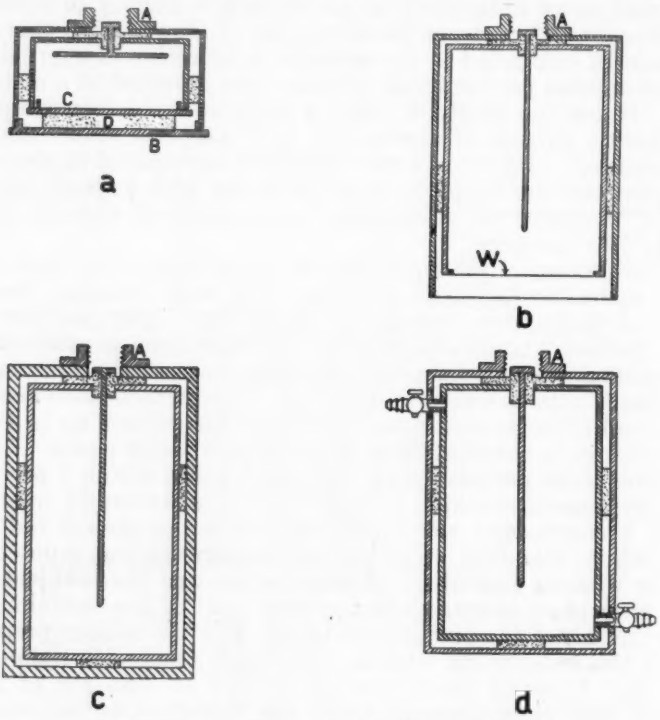


FIGURE 3.—*Types of ionization chambers.*

a, α-ray chamber; *b*, β-ray chamber; *c*, γ-ray chamber; *d*, emanation chamber.

plate of this chamber is made of two parts separated by an insulating disk, *D*. The upper part is a metal tray, *C*, formed to close the lower end of the chamber when the lower metal disk, *B*, is screwed into the grounded case of the chamber. The active material is placed in the metal tray. A β-ray chamber is shown at *b*. The proportions are changed from that of the α-ray chamber to take advantage of the longer ionizing paths of β rays. The radiation is admitted through the thin aluminum window, *W*, which closes the lower end of the chamber. For measurement of γ radiation a chamber surrounded by a lead shield, as shown at *c*, may be used. It is also possible to adapt this apparatus for the emanation measurements by the use of a chamber as sketched at *d*.

The use of interchangeable chambers is of considerable advantage when working with material which may contaminate the chamber or in cases of accidental contamination. By providing a reserve chamber the contaminated chamber may be replaced at once when a sudden release of the contaminating material renders a chamber temporarily useless. Since the chambers may be so designed as to afford a possibility of thorough cleaning, those which have become contaminated may be renovated at leisure.

VI. ACKNOWLEDGMENTS

The writer wishes to acknowledge the assistance of B. W. Brown and L. L. Stockman for help in constructing and calibrating an amplifier as described above. It is also a pleasure to acknowledge considerable help in the design of the amplifier from Dr. A. V. Astin and Dr. G. W. Gardiner.

WASHINGTON, February 16, 1933.

167156—33——2

"TIN-FREE" LEADED BEARING BRONZE

By H. K. Herschman and J. L. Basil

ABSTRACT

A study was made of the effect of small proportions of various elements on the distribution of lead in leaded bronzes containing more than 30 percent lead. The mechanical properties believed to be significant in the service of a bearing were determined at several different temperatures for leaded bronzes developed in the course of this investigation and which contained 30.5 to 40 percent lead, together with small amounts of sulphur, silicon, and zirconium. The mechanical properties of several commercial leaded bronzes containing 26 to 40 percent lead were also determined. Service tests were made on a set of connecting-rod and main bearings of the sulphur-silicon-zirconium leaded bronze installed in a Wright type J–5 airplane engine.

CONTENTS

	Page
I. Introduction	591
II. Factors affecting the distribution of lead in leaded bronzes	592
1. Constitution of copper-lead alloys	592
2. Composition of alloys prepared	593
3. Preparation of alloys	593
4. Metallographic examination and discussion	594
III. Mechanical properties	596
1. Preparation of alloys	596
2. Apparatus and tests	596
(*a*) Resistance to wear	596
(*b*) Compressive strength	597
(*c*) Single-blow impact value	598
(*d*) Resistance to pounding	598
3. Results and discussion	598
(*a*) Resistance to wear	598
(*b*) Compressive strength	599
(*c*) Single-blow impact resistance	602
(*d*) Resistance to pounding	602
IV. Service tests	606
V. Summary	606
VI. Acknowledgments	608

I. INTRODUCTION

The development of greater power and higher speeds in internal-combustion engines and in other machines necessitates the use of bearing alloys with mechanical properties at elevated temperatures exceeding those of the usual white-metal bearing alloys in addition to the essential properties of any satisfactory bearing metal. Lead-copper aggregates, consisting of lead dispersed in a matrix of copper or a copper-base alloy, have shown promise and have had some application in meeting these increasing demands. In this report these lead-copper aggregates are referred to as leaded bronzes. Bronzes containing 25 to 28 percent or more lead have to a great extent replaced tin-base alloys in connecting-rod bearings of airplane engines.

Commercial leaded bronzes of high lead content generally contain tin. The tin is added to prevent the agglomeration and segregation of lead particles and to strengthen the matrix of the alloy. The usual maximum lead content of commercial leaded bronzes prepared by ordinary foundry methods is about 28 percent. Segregation of lead is usually excessive in alloys containing 30 percent or more of lead.

The primary purpose of the work reported in this paper was to develop a leaded bronze of high lead content, containing no tin or other strategic metals,[1] which could replace the usual tin-base-bearing alloys in many fields of service. The investigation, which was sponsored by the War Department, comprised two phases, (1) a study of the effect of small proportions of various elements on the distribution of lead in leaded bronzes containing more than 30 percent lead, and (2) the determination of the characteristic mechanical properties of leaded bronzes containing 30.5 to 40 percent of lead, together with small amounts of sulphur, silicon, and zirconium. The mechanical properties of several commercial leaded bronzes containing from 26 to 40 percent lead were also determined.

Service tests were also made on a series of steel-backed bearings lined with one of the more promising of the alloys developed during the course of this investigation, namely, a copper-lead-bearing metal treated with sulphur, silicon, and zirconium. These service tests were made on bearings installed in a Wright type J-5 airplane engine which was run on an engine test block.

II. FACTORS AFFECTING THE DISTRIBUTION OF LEAD IN LEADED BRONZES

1. CONSTITUTION OF COPPER-LEAD ALLOYS

The solubility of lead in copper in the solid state is negligible. Recently, Claus [2] showed that copper-lead mixtures containing 37 to 38 percent lead are completely miscible above 950° C. A melt of this composition when cooled slightly below this temperature consists of a solid phase containing over 95 percent copper and a liquid phase which is relatively pure lead. Unless cooled very rapidly through the freezing range, the liquid phase of nearly pure lead coalesces into relatively large masses during the freezing and the aggregate at room temperature shows marked segregation of lead. The freezing of homogeneous melts containing less than 38 percent lead is similar to the example just given except that the temperature at which the relatively pure copper separates from the melt exceeds 950° C. in proportion to the decrease of the lead content below 38 per cent. Thus, in alloys containing the lower proportions of lead, there is formed during freezing a more continuous network of copper before the liquid phase becomes nearly pure lead and, as a consequence, the tendency toward segregation of lead is not so great in these alloys.

The problem is further complicated by the fact that alloys containing more than 38 percent lead, when melted, consist of two immiscible liquid phases and the lead is therefore already segregated even in the liquid phases before any restraining network of a solid phase can form.

[1] Roger Taylor, Strategic Raw Materials, Metals and Alloys, vol. 1, p. 5, 1929

[2] W. Claus, Zur Kenntnis des System Kupfer-Blei und verwandter heterogener Systems, Zeit. f. Metallkunde, vol. 23, no. 9, p. 264, September 1931.

2. COMPOSITION OF ALLOYS PREPARED

Suppression of lead segregation in lead-copper aggregates which are cooled rather slowly, as in sand castings, can sometimes be accomplished by the addition to the alloy of small proportions of certain elements. In order to determine the elements which are effective in this respect for leaded bronzes containing approximately 35 and 50 percent lead, a series of alloys of the compositions shown in table 1 was prepared.

TABLE 1.—*Compositions and casting temperatures of leaded bronzes with additions of elements to effect dispersion and distribution of lead*

Alloy	Copper [1]	Lead [1]	Added elements [1]	Percent	Casting temperature
	Percent	*Percent*			°C.
B	64	35	Tin	1	1,100 (2,010° F.)
C	49.5	49.5	do	1	1,100 (2,010° F.)
H	64	35	Manganese	1	1,100 (2,010° F.)
J	49.5	49.5	do	1	1,100 (2,010° F.)
L	61.5	33.5	do	5	1,100 (2,010° F.)
M	47.5	47.5	do	5	1,100 (2,010° F.)
N	64.5	34.5	Calcium	1	1,100 (2,010° F.)
P	49.5	49.5	do	1	1,100 (2,010° F.)
Q	63.5	34.5	do	2	1,100 (2,010° F.)
S	64.5	34.5	Barium	1	1,100 (2,010° F.)
T	49.5	49.5	do	1	1,100 (2,010° F.)
W	63	34	Magnesium	3	1,100 (2,010° F.)
X	64	34.5	do	1.5	1,100 (2,010° F.)
Y	49.5	49	do	1.5	1,100 (2,010° F.)
A-1	64.5	34.5	Aluminum	1	1,100 (2,010° F.)
B-1	49.5	49.5	do	1	1,100 (2,010° F.)
A-2	64.5	34.5	Nickel	1	1,100 (2,010° F.)
B-2	49.5	49.5	do	1	1,100 (2,010° F.)
A-3	64.4	34.6	Silicon	1	1,100 (2,010° F.)
B-3	49.5	49.5	do	1	1,100 (2,010° F.)
A-4	64.4	34.6	Zirconium	1	1,100 (2,010° F.)
B-4	49.5	49.5	do	1	1,100 (2,010° F.)
A-6	65	35	Lithium	0.05	1,100 (2,010° F.)
B-6	50	50	do	0.05	1,100 (2,010° F.)
A-8	64.5	34.5	Silicon-zirconium alloy	[2] 1.5	1,100 (2,010° F.)
B-8	49.5	49.5	do	1.5	1,100 (2,010° F.)
A-9	64.5	34.5	Titanium	1	1,100 (2,010° F.)
B-9	54.5	44.5	do	1	1,140 (2,085° F.)
B-14	54.5	45	Sulphur	0.4	960 (1,760° F.)
B-17-1	54.5	44.5	do	0.4	990 (1,815° F.)
			Silicon-zirconium alloy	[2] 1	
B-19-0	54	44	Sulphur	0.4	960 (1,760° F.)
			Silicon-zirconium alloy	[2] 1.5	
B-22-0-9	54.5	44.5	Sulphur	0.4	950 (1,740° F.)
			Silicon-zirconium alloy	[2] 0.5	
B-23-0-9	53.5	44	Sulphur	0.4	950 (1,740° F.)
			Silicon-zirconium alloy	[2] 2	

[1] Nominal compositions.
[2] The silicon-zirconium alloy is a commercial product containing approximately 55 percent zirconium, 38 percent silicon, 5 percent iron, and small amounts of aluminum and carbon.

3. PREPARATION OF ALLOYS

Heats, 6 to 8 pounds each, of the desired compositions, melted in a gas-fired furnace in clay-graphite crucibles, were cast in green sand molds. The castings were cylindrical, 2½ inches long by 1¼ inches in diameter as shown in figure 1. (A few specimens were 3 inches by three fourths inch in diameter.) In each case, the metal was heated 100° to 125° C. (212° to 255° F.) above the desired casting temperature (table 1), thoroughly stirred while cooling to the casting

temperature and then poured. The heats were deoxidized by phosphorus-copper added shortly before casting.

Most of the elements added to influence the dispersion of lead were added directly to the melt. Some were added in the form of alloys or "hardeners", usually containing about 10 percent of the "addition" element alloyed with 90 percent copper, prepared beforehand in a high-frequency induction furnace. The elements added in this manner were titanium, nickel, silicon, zirconium, and silicon-zirconium alloy. Manganese was added as a 70–30 copper-manganese alloy. Sulphur was added both as roll sulphur and as lead sulphide.

4. METALLOGRAPHIC EXAMINATION AND DISCUSSION

The castings were sectioned longitudinally and polished for metallographic examination. Lead can be detected readily in an unetched polished copper matrix. Hence the specimens were examined in the

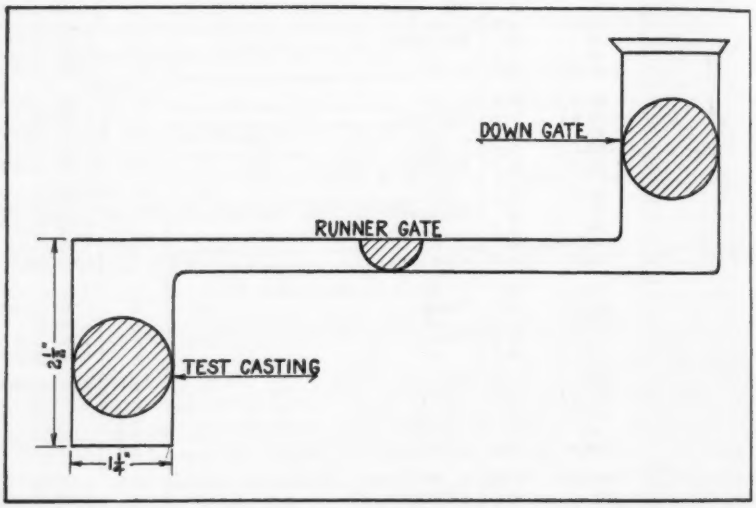


FIGURE 1.—*Form of casting for determining the effect of added elements on distribution of lead in leaded bronzes.*

unetched condition, since the metallographic study was primarily made to determine the manner in which lead was distributed.

The various "addition" elements, on the evidence given by the specimens examined, were grouped as follows:

1. Those which had a negligible effect in preventing segregation of the lead. The distribution of the lead in typical examples is shown in figure 2.

2. Those which aided in obtaining uniformity of distribution of the lead, but which did not prevent the lead from forming continuous envelopes around the grains of the copper-rich phase which thus destroyed the continuity of the matrix (fig. 3).

3. Those which prevented segregation and aided in dispersing the lead as discontinuous particles, a condition which favors continuity of the copper-base ground mass (fig. 4).

Obviously, the "addition" elements of group 1 are undesirable. Elements of group 2 may be considered as partially beneficial, but

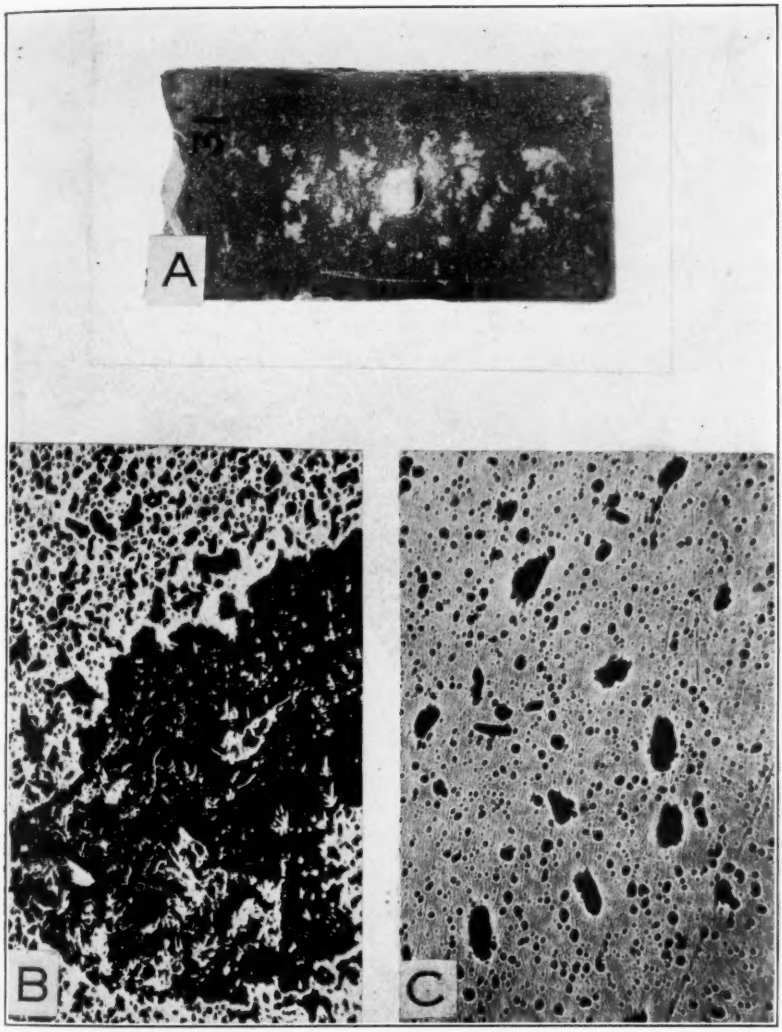


FIGURE 2.—*Typical structures of specimens in which additions were ineffective in preventing lead segregation.*

The heats from which these specimens were cast contained 45 percent lead. *A*, Lighter areas show typical appearance of segregated lead. × 1. *B*, Typical appearance of areas in region of heavy segregation of lead. Lead is represented by dark areas. × 50. Unetched. *C*, Typical appearance of "lead-poor" areas in regions free from segregation. Lead is represented by dark areas. × 50. Unetched.

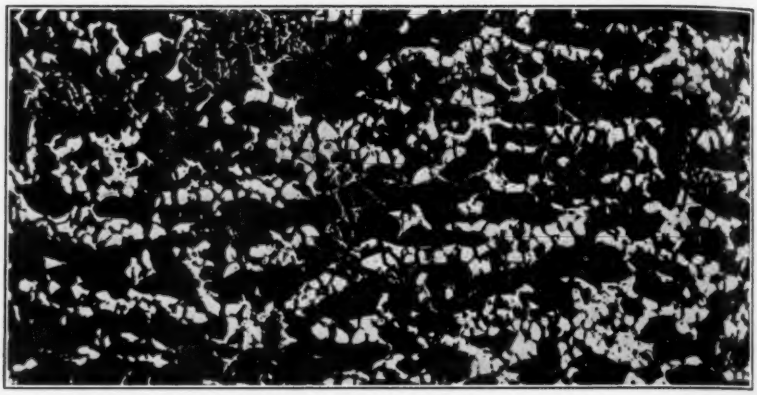


FIGURE 3.—*Microstructure of a bronze containing approximately 45 percent lead, 0.4 percent sulphur, and remainder copper, in which the lead, represented by the dark areas, was distributed uniformly, but in such manner as to break the continuity of the copper-base material, thus destroying its supporting effect.* × *50. Unetched.*

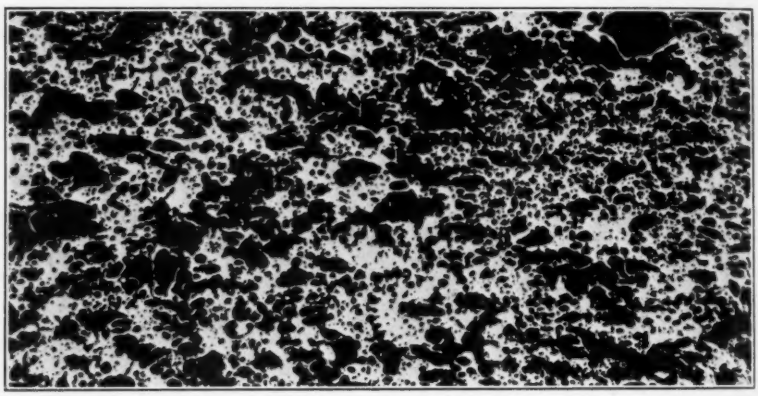


FIGURE 4.—*Structure of a bronze containing approximately 44 percent lead, 0.4 percent sulphur, 1.5 percent silicon-zirconium alloy, and remainder copper, showing the lead, represented by the dark areas, distributed as discontinuous areas, thus permitting a continuous copper-base matrix.* × *50. Unetched.*

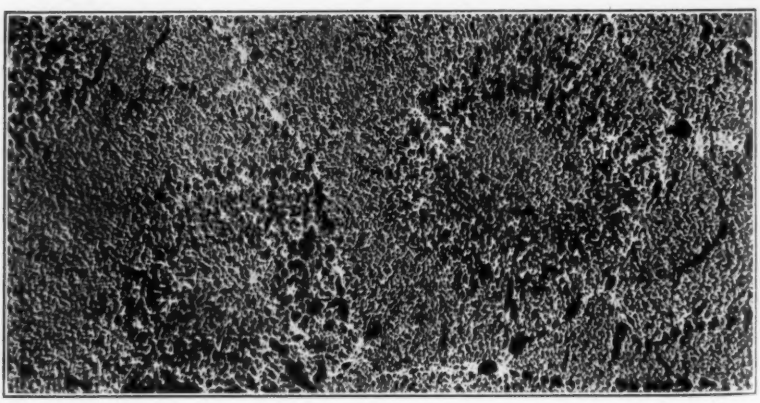


FIGURE 5.—*Microstructure of a bronze containing about 35 percent lead and 1 percent silicon showing the dispersion of the lead, represented by the dark areas, in an area of specimen which was free of lead segregation.* × *50. Unetched.*

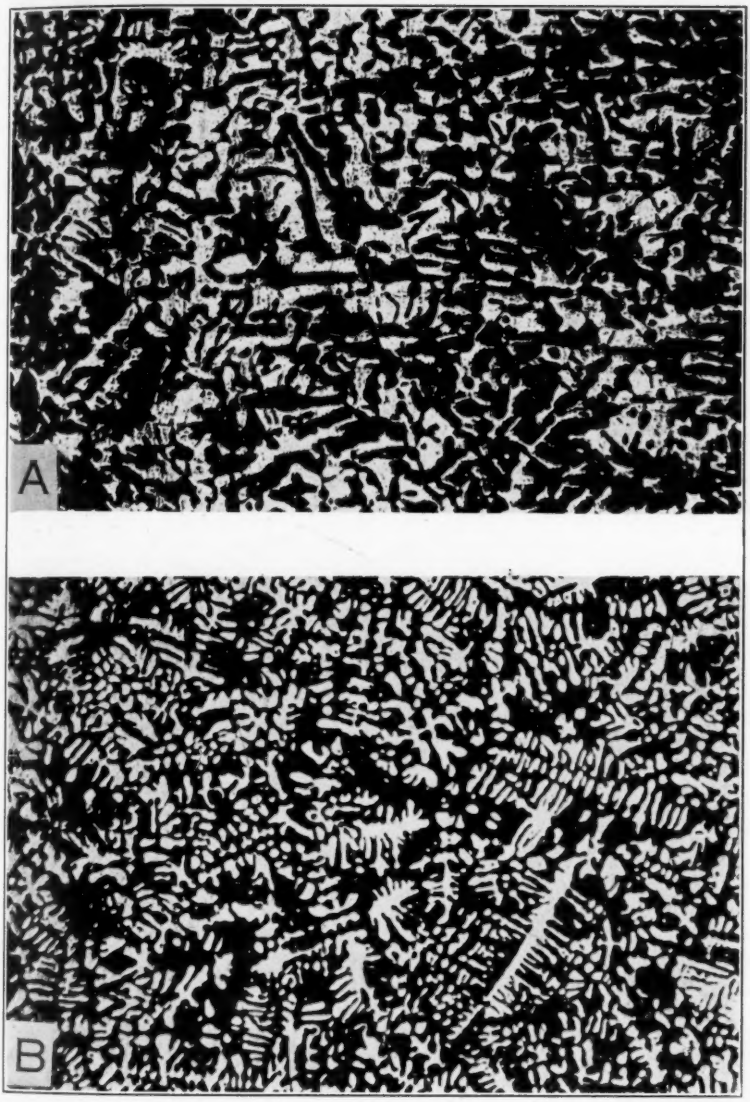


FIGURE 6.—*Microstructures of bronzes containing about 34.5 percent lead and different additions of calcium showing the dispersion of the lead, represented by dark areas.* × *50. Unetched.*

A, 1 percent calcium. *B*, 2 percent calcium.

LIBRARY OF CONGRESS

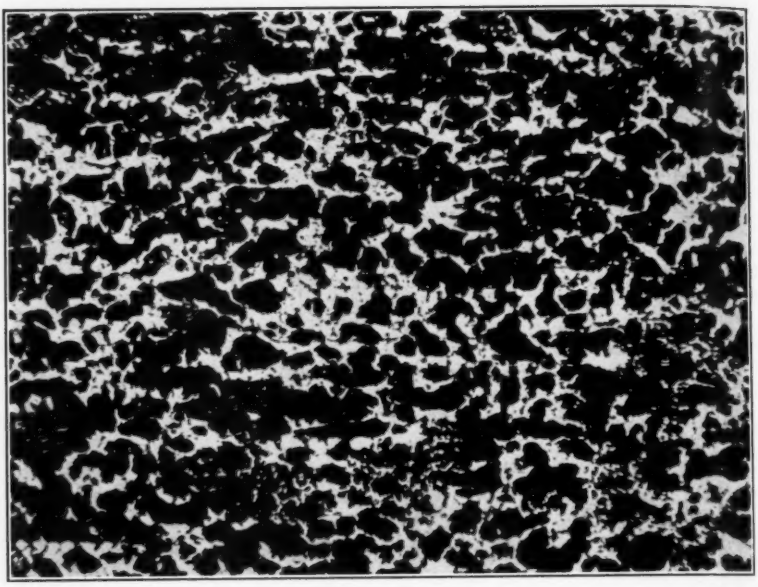


FIGURE 7.—*Microstructure of specimen containing about 55 percent copper, 45 percent lead, and 0.4 percent sulphur.* × *50.*

The lead is represented by the dark areas. Unetched.

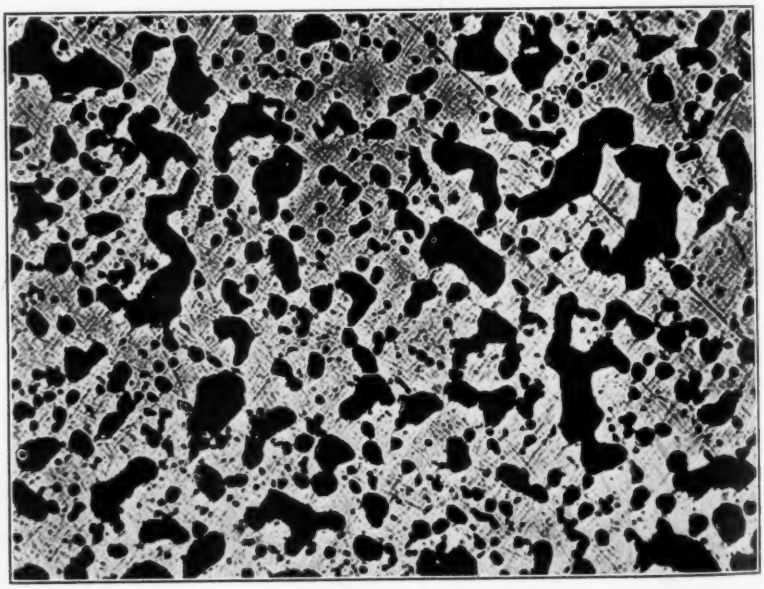


FIGURE 8.—*Microstructure of casting containing about 64.5 percent copper, 34.5 percent lead, and 1 percent zirconium.* × *50.*

The lead is represented by the dark areas. Unetched.

cannot be considered entirely satisfactory on account of loss of continuity and strength of the copper-rich matrix. The most effective and desirable addition elements are those of group 3. Obviously, a wide variety of microstructures can be obtained in high-lead bronzes by suitable variations in the casting conditions. The results here discussed refer only to specimens cast under the conditions described.

The "addition" elements which, in the amounts used in this work, had no marked beneficial effect on the distribution of lead in leaded bronzes containing 35 percent or more lead included the following: Lithium, 0.05 percent; magnesium, 1.5 and 3 percent; aluminum, titanium and tin, 1 percent each; manganese, 1 and 5 percent; and nickel, 1 percent. Although the addition of silicon was not entirely beneficial, since considerable segregation of lead was observed at the bottom of the casting, its use did result in unusual dispersion of the lead in the areas free of segregation (fig. 5).

Either calcium or sulphur aided in distributing the lead uniformly, but failed to prevent the formation of continuous lead envelopes around the copper-rich grain (fig. 3). Although a few small segregated areas were observed in specimens containing approximately 34.5 percent lead, treated with 1 and 2 percent calcium, respectively, they were not of such magnitude as to be considered serious. These specimens showed exceptional uniformity in the distribution of the lead as shown in figure 6. The melts treated with calcium drossed very severely on account of the rapidity with which calcium oxidizes. The alloy containing 2 percent of calcium was very brittle.

The use of sulphur for preventing segregation in leaded bronzes has long been known.[3] The effectiveness of sulphur has been attributed to its ability to decrease the range of immiscibility of copper and lead in the liquid state.[4] A sand-cast specimen containing approximately 55 percent copper, 45 percent lead, and 0.4 percent sulphur showed unusually uniform distribution of the lead (fig. 7).

Zirconium and barium added separately, promoted the dispersion of lead in the manner described under group 3. Castings which contained 34.5 percent lead and 1 percent zirconium were free of lead segregation. Castings prepared from a melt of similar lead content treated with 1 percent barium showed a few small, almost negligible, areas of segregation. Although the barium was added as metallic barium sheathed in copper to prevent oxidation, it "burned out" to some extent during heating and caused excessive drossing. The lead distribution in these specimens, as shown in figures 8 and 9, was fairly satisfactory. However, neither zirconium nor barium was effective in preventing segregation in castings made from bronze containing 49.5 percent lead.

Although the addition of sulphur resulted in very uniform distribution of the lead, its use was not entirely satisfactory because it destroyed the continuity of the copper matrix (fig. 7) which caused the bronze castings to have low compressive strength. Zirconium and barium, on the other hand, had shown a marked ability to disperse the lead in bronzes containing up to 35 percent lead. It

[3] A. Allan, Jr., The Patent Controversy Over Bearing Metals (9th and 11th papers), Metal Industry (N.Y.), vol. 9, pp. 155 and 295, 1911.
[4] W. M. Corse, Bearing Metals and Bearings, Am. Chem. Soc. Monograph Series No. 53, Chemical Catalog Co., New York, N.Y.

would seem reasonable, therefore, that either or both of these elements when added with sulphur to a high-lead bronze should give the desired type of lead distribution. Barium proved to be unsatisfactory, because of the rapidity with which it oxidized and combined with sulphur to form a slag which largely eliminated both added elements. The present cost and availability of metallic zirconium makes its use for other than experimental purposes almost prohibitive. For further experimental work, therefore, a commercial alloy of zirconium and silicon was substituted. This alloy contained about 55 per cent zirconium, 38 percent silicon, 5 percent iron, and less than 2 percent aluminum. The presence of silicon in this alloy seemed desirable. Silicon itself did not prevent segregation, but because of its dispersive power as illustrated in figure 5, there was reason to expect that it would be useful in combination with either zirconium or zirconium and sulphur. Several combinations of these elements were used as additions to leaded bronze containing 35 and 45 percent lead. The sulphur was varied from 0.1 to 0.5 percent and the silicon-zirconium alloy from 0.5 to 2 percent. It was found that the best distribution and dispersion of the lead was obtained by the use of the combined addition of 0.4 percent sulphur and 1 to 1.5 percent silicon-zirconium alloy. The effect of additions of 1 and 1.5 percent silicon-zirconium alloy on the microstructures of specimens containing approximately 54 percent copper, 45 percent lead, and 0.4 percent sulphur are shown in figures 10 and 4, respectively.

III. MECHANICAL PROPERTIES

1. PREPARATION OF ALLOYS

The mechanical properties, believed to be of significance in the service of a bearing, were determined on a series of sulphur-silicon-zirconium-treated copper-lead alloys.[5] The alloys containing these addition elements showed the best dispersion of the lead. In order to study the effect on the mechanical properties of various percentages of silicon-zirconium-alloy additions, alloys of the compositions shown in table 3 were prepared as 80-pound heats in a high-frequency induction furnace. This furnace was used primarily for convenience.

After the various constituents of each alloy were added, the melt was heated sufficiently to insure thorough alloying. The heat was then allowed to cool to approximately 950° C. (1,740° F.) and cast in closed green sand molds in shapes as later described under the discussion of each specific test.

2. APPARATUS AND TESTS

(a) RESISTANCE TO WEAR

The resistance to wear was determined on the Amsler universal wear testing machine modified for the testing of soft alloys as described in a previous publication.[6] The test specimens, which were cast as "tires" on the peripheries of steel rings, were run against reference specimens of SAE 1045 steel treated to a hardness of 240

[5] H. K. Herschman and J. L. Basil, Copper-lead Alloys, U.S. Patent No. 1895261, 1932.
[6] H. K. Herschman and J. L. Basil, Mechanical Properties of White Metal Bearing Alloys at Different Temperatures, Proc. ASTM, vol. 32, pt. 2, p. 536, 1932.

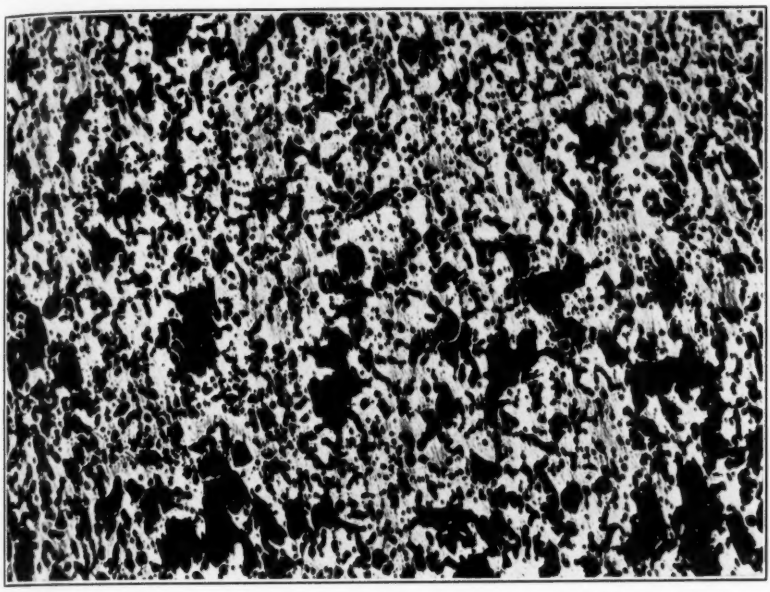


FIGURE 9.—*Microstructure of leaded bronze casting containing approximately 64.5 percent copper, 34.5 percent lead, and 1 percent barium.* × *50.*

The lead is represented by the dark areas. Unetched.

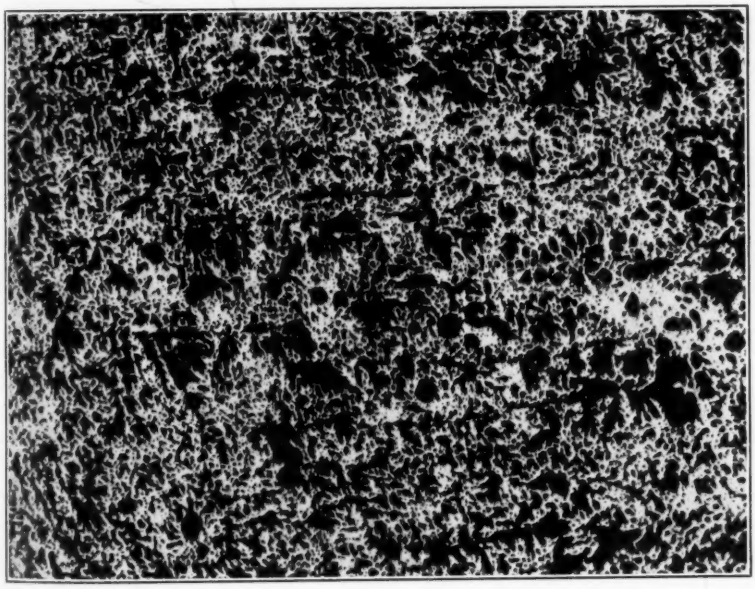


FIGURE 10.—*Microstructure of leaded bronze casting containing approximately 54 percent copper, 44.5 percent lead, 0.4 percent sulphur, and 1 percent silicon-zirconium alloy.* × *50.*

The lead is represented by the dark areas. Unetched.

UNIV. OF MICH.

Brinell. Pressure was obtained at the area of contact between the specimens by applying a load of 10 pounds on the steel reference specimen. A stream of kerosene was directed on the test specimen near its area of contact with the reference specimen to provide partial lubrication and to cool the specimens. Tests were made at approximately 20° C. only.

The wear-resistance tests were made on commercially available leaded bronzes of high lead content[7] and on alloy B–21[8] of the compositions shown in table 2. The thickness of the bronze layer or "tire" cast on the steel back, after "finish-machining", did not exceed 0.015 inch.

TABLE 2.—*Compositions of commercially available leaded bronzes and of sulphur-silicon-zirconium-treated leaded bronze used in wear tests*

Specimen No.	Copper	Lead	Tin	Other constituents
	Percent	*Percent*	*Percent*	*Percent*
1-53 [1]	70	30	(2)	
P-6 [1]	70	24	6	
76-24 [1]	76	24	(2)	
60-40	[1] 61	[3] 39.1	(2)	
70-30	[1] 65.5	[3] 34.6	(2)	
1-70 [4]	69.3	30.59	--------	0.11 nickel and zinc.
72-5 [4]	69.46	28.48	1.78	.28 nickel and zinc.
75-4 [4]	68.23	26.20	4.96	.61 nickel and zinc.
B-21-1 [3]	66.5	31.5	--------	Silicon-zirconium alloy 1.5.[1] Sulphur 0.4.[1]

[1] Nominal compositions.
[2] Tin not reported.
[3] Determinations made by J. A. Scherrer, Bureau of Standards.
[4] Analysis made by The Bohn Aluminum & Bronze Co., Detroit, Mich.

(b) COMPRESSIVE STRENGTH

The apparatus and procedure for making compression tests were identical with those described in a previous publication.[9] The tests were made at approximately 20°, 100°, 150°, 200°, and 250° C. (68°, 212°, 300°, 390°, and 480° F.). The loads were applied in increments of 100 pounds, this increment being equivalent to an increase in stress of 500 lbs./in.^{2}. The speed of the crosshead of the machine was approximately 0.04 inch per minute. This low rate of speed was used as it permitted closer regulation of loading than would have been possible with the next higher speed available on the machine used.

The compression test specimens were made of only the five alloys listed in table 3. Alloys B-14, B-22, B-17, and B-21 (table 3) were prepared as castings five eighths inch in diameter by 4 inches long and alloy "C" (table 3) was purchased in the form of bars three fourths inch in diameter by 12 inches long. The "finish-machined" specimens were 0.505 inch diameter by 1 inch long.

[7] The specimens of commercial leaded bronzes were furnished through the courtesy of the Allison Engineering Co., of Indianapolis, Ind.; and the Bohn Aluminum & Brass Co., Detroit, Mich.
[8] The specimens were furnished through the courtesy of Wright Field, War Department. They were prepared at a commercial plant from alloy ingots prepared by the Bureau of Standards.
[9] See footnote 6, p. 596.

TABLE 3.—*Composition of leaded bronzes prepared for compression, single blow charpy, impact and pounding tests* [1]

Heat designation	Copper	Lead	Silicon-zirconium alloy [1]	Sulphur [1]	Antimony
	Percent	*Percent*	*Percent*	*Percent*	*Percent*
B-14	[2] 59.3	40.3	.....	0.4	.....
B-22	[2] 57.4	41.7	0.5	.4	.....
B-17	65.4	33.2	1.0	.4	.....
B-21-2	[2] 62.1	36.0	1.5	.4	.....
"C" [3 4]	73.75	26.0	.....	.....	0.25

[1] Amounts added to the heats.
[2] Copper determined by difference.
[3] Commercial leaded bronze.
[4] Pounding tests were not made on alloy "C."

(c) SINGLE-BLOW IMPACT VALUE

The single-blow impact resistance was determined with a Charpy impact machine of 224.1 foot-pound capacity. The tests were made at 20°, 100°, 150°, 200°, and 250° C. (68°, 212°, 300°, 390°, and 480° F.). The specimens tested above room temperature were heated in an electric muffle furnace, held at temperature for 15 minutes, then transferred to the machine and tested. Not more than three seconds were required for the last step. The heat loss during transference has been previously found to be negligible.[10] The specimens as cast were ⅝-inch square by 4 inches long. The "finish-machined" specimen conformed with the design recommended for the Charpy impact test in the Proposed Method for Impact Testing of Metallic Materials of the American Society for Testing Materials.[11]

(d) RESISTANCE TO POUNDING

The apparatus and the procedure for the pounding tests have been described in a previous publication.[12] Tests were made at 20°, 100°, 150°, 200°, and 250° C. (68°, 212°, 300°, 390°, and 480° F.). The cylindrical specimens, 0.394 inch in diameter by 0.985 inch long (10 by 25 mm), were machined from castings five eighths inch in diameter by 4 inches long.

3. RESULTS AND DISCUSSION

(a) RESISTANCE TO WEAR

The results of the wear tests are shown graphically in figure 11. Alloys B-21-1, 70-30, P-6, and 75-4 (table 2) had about the same rates of wearing after the "wearing-in period"; that is, after the first 10,000 to 20,000 revolutions. Alloys 75-4 and P-6 contained approximately the same amounts of lead and about 5 and 6 percent tin, respectively. The former also contained small proportions of nickel and zinc. Alloy 70-30 contained about 34.5 percent lead as compared with 31.5 percent in alloy B-21-1. Alloy 72-5, which contained about 28.5 percent lead, 1.75 percent tin, and a small percentage of nickel and zinc had a perceptibly higher rate of wear than the four alloys just considered. Specimens 1-53, 76-24, 1-70, and 60-40 (table 2) which were reported by the manufacturers to contain only

[10] G. Willard Quick, The Resistance to Impact of Rail Steels at Elevated Temperatures, B.S. Jour. Research, vol. 8 (RP409), p. 191, 1932.
[11] Proc., Am. Soc. Testing Materials, vol. 26, pt. 1, p. 553, 1926.
[12] See footnote 6, p. 596.

copper and lead, the latter element in amounts varying from 24 to 40 percent, had comparatively high rates of wear.

(b) COMPRESSIVE STRENGTH

The relation of stress to strain in compression at the various test temperatures for each of the alloys listed in table 3 is shown in figures 12, 13, 14, 15, and 16.

By using the least count of the extensometer as the criterion for the "departure from a straight line",[13] it was possible to determine

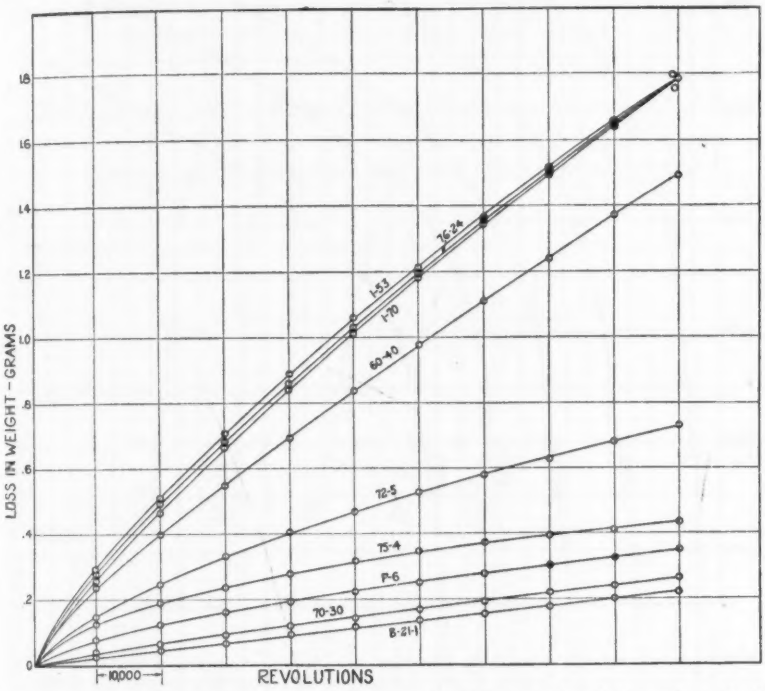


FIGURE 11.—*Relation between wear, as determined by loss of weight, and revolutions for leaded bronze bearing alloys tested on Amsler wear testing machine.*

The bronzes were cast on the peripheries of steel rings. All specimens were prepared in commercial foundries.

All alloys were tested against SAE No. 1045 steel heat-treated to give a Brinell hardness number of 240. The numbers on the curves are the specimen numbers listed in the table of compositions (table 2).

approximately the limits of proportionality of stress and strain at room temperature (figs. 12 to 16, inclusive). This determination became increasingly difficult and questionable, however, as the temperature of test increased, particularly for alloys B-14 and B-22. Hence, in order to show graphically the effect of temperature, an arbitrary value for strain was selected, namely, 0.3 percent, which was considered to represent the relative yield strength.[14] The stresses

[13] Discussion by L. B. Tuckerman of paper by R. L. Templin, "The Determination and Significance of the Proportional Limit in the Testing of Materials", Proc. Am. Soc. Test. Mats., vol. 29, pt. 1, p. 538, 1929.

[14] ASTM tentative specification E-8-32T, vol. 32, pt. 1, p. 955.

necessary to produce deformations of 0.3 percent as determined from figures 12 to 16 are shown in figure 17.

The results of the compression tests indicated that alloy B-21-2 (table 3) which was treated with sulphur and silicon-zirconium alloy and contained 36 percent lead, was capable of sustaining loads comparable with those sustained by the commercial alloy "C", which contained only 26 percent lead. Alloy B-21-2 had at 100° C. (212° F.)

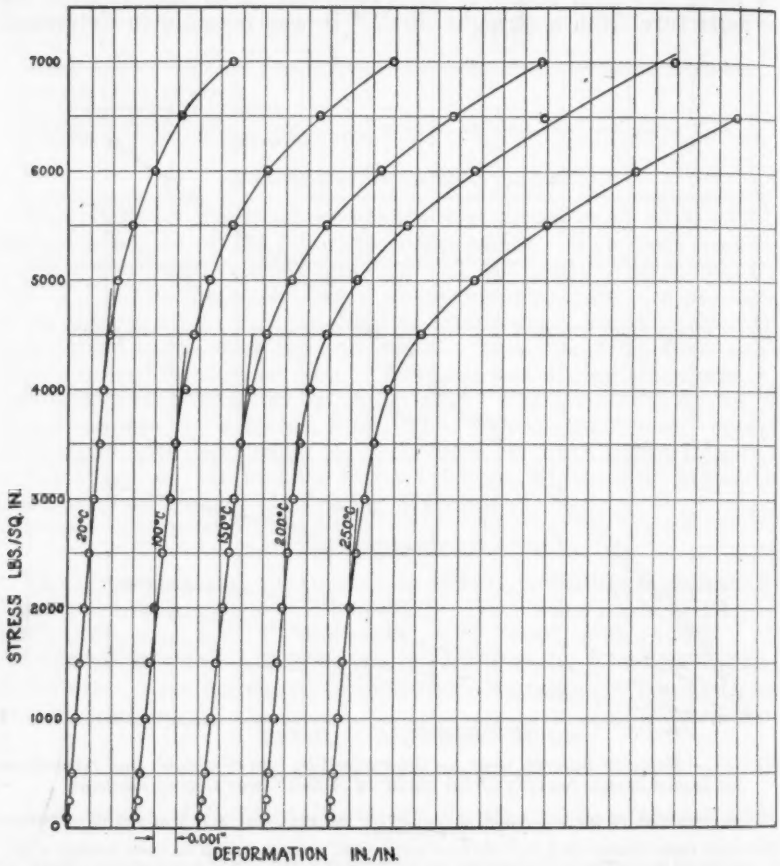


FIGURE 12.—*Stress-strain relation in compression tests at various temperatures for commercial alloy "C" (copper, 73.75 percent; lead, 26 percent; and antimony 0.25 percent).*

Each plotted point represents an average of two determinations.

a yield strength slightly higher than that determined at room temperature. This was unusual and the results were checked with specimens of similar composition prepared from another heat. The results although not included in this report, verified the increase shown in figure 17. A few preliminary experiments also indicated that specimens of this composition after being heated at 90° to 100° C. for a period of 15 hours and then cooled to room temperature, possessed

higher compressive strength at room temperature than before being treated, which indicates that this alloy may be adaptable to age hardening treatments. Alloys B-17, B-22, and B-14, which contained 0.4 percent sulphur and silicon-zirconium alloy up to 1 percent, had only about half the compressive strength of alloy B-21-2 treated with

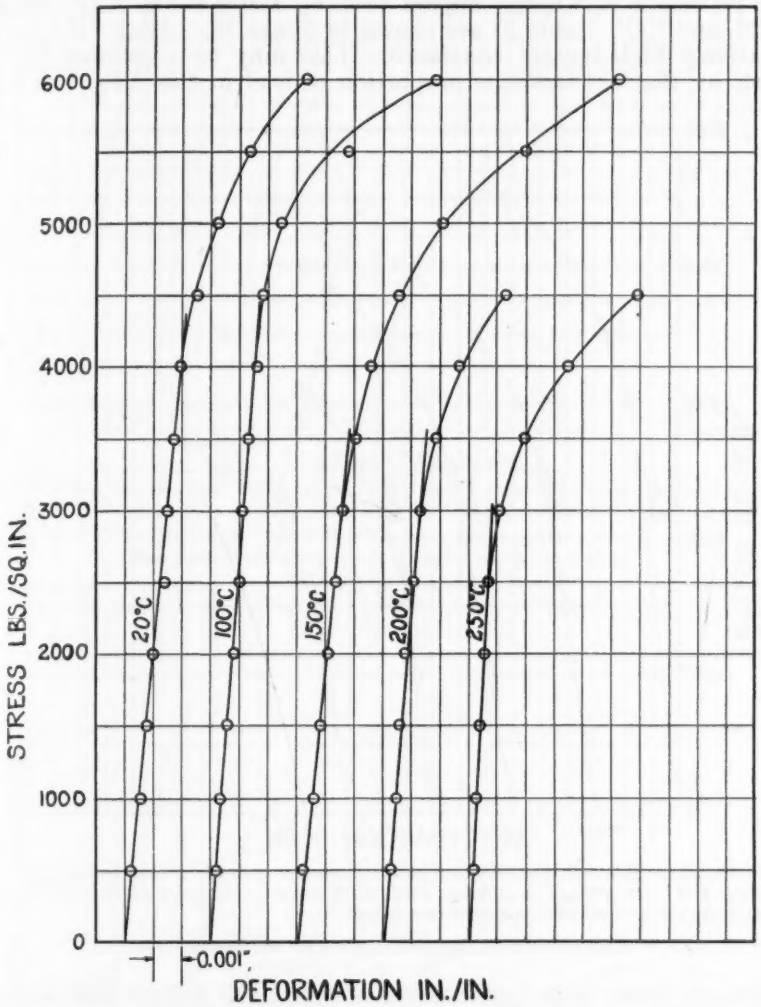


FIGURE 13.—*Stress-strain relation in compression tests at various temperatures for alloy B-21-2 (copper, 61.2 percent; lead, 36 percent, treated with 0.4 percent sulphur and 1.5 percent silicon-zirconium alloy).*

Each plotted point represents an average of two determinations.

0.4 percent sulphur and 1.5 percent silicon-zirconium alloy, and alloy "C", a commercial leaded bronze containing 0.25 percent antimony. Particularly to be noted (fig. 17), is the difference between the effect of the addition of 1.5 percent of silicon-zirconium alloy in alloy B-21-2 and the effect of the addition of 1 percent of silicon-zirconium alloy

in alloy B-17. The slightly greater addition of silicon-zirconium alloy resulted in a marked increase in yield strength of the leaded bronze at all temperatures up to 250° C.

(c) SINGLE-BLOW IMPACT RESISTANCE

The results of Charpy impact tests on alloys B-14, B-17, B-21-2, B-22, and "C" (table 3) are shown in figure 18. Alloy "C" had a relatively high impact resistance. This may be accounted for, in part, by the fact that the proportion of lead in this alloy was considerably lower than in the other alloys. The impact resistance of B-21-2, appeared to be only slightly affected by temperature.

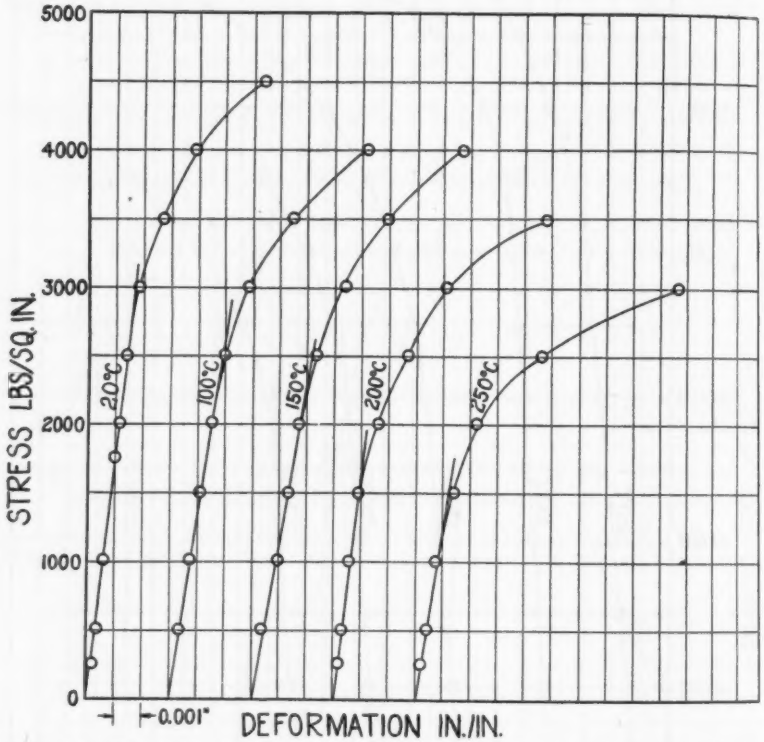


FIGURE 14.—*Stress-strain relation in compression tests at various temperatures for alloy B-17 (copper, 65.4 percent; lead, 33.2 percent, treated with 0.4 percent sulphur and 1 percent silicon-zirconium alloy).*

Each plotted point represents an average of two determinations.

(d) RESISTANCE TO POUNDING

The pounding tests measured the deformation of the specimens previously described, resulting from repeated blows from a 2-pound hammer or tup falling freely through a distance of 2 inches. Figure 19 shows the relationship at 20°, 100°, 200°, and 250° C. (68°, 212°, 390°, and 480° F.) of the number of blows of the hammer to the resulting deformation for alloys B-14, B-22, B-17, and B-21-2 listed in

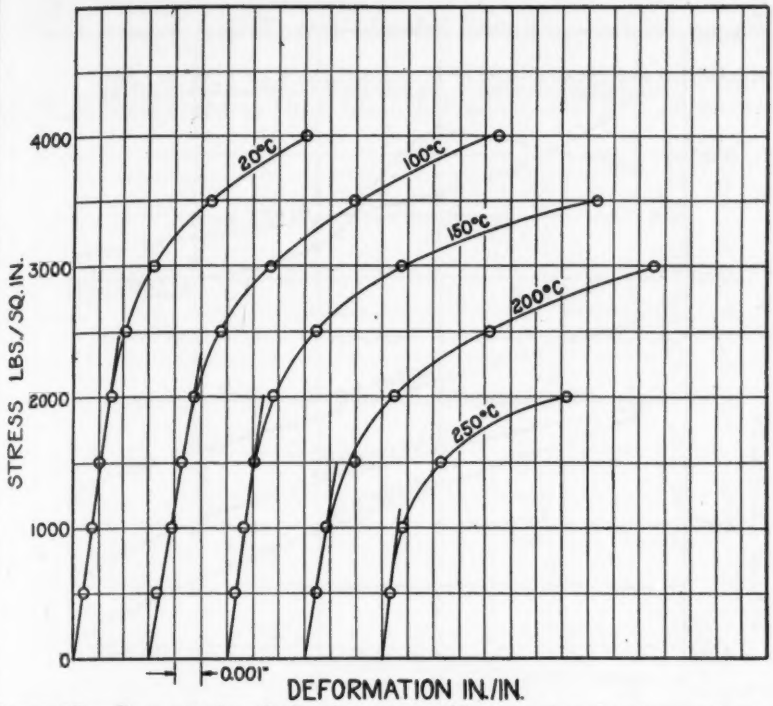


FIGURE 15.—*Stress-strain relation in compression tests at various temperatures for alloy B-22 (copper, 57.4 percent; lead, 41.7 percent, treated with 0.4 percent sulphur and 0.5 percent silicon-zirconium alloy).*

Each plotted point represents an average of two determinations.

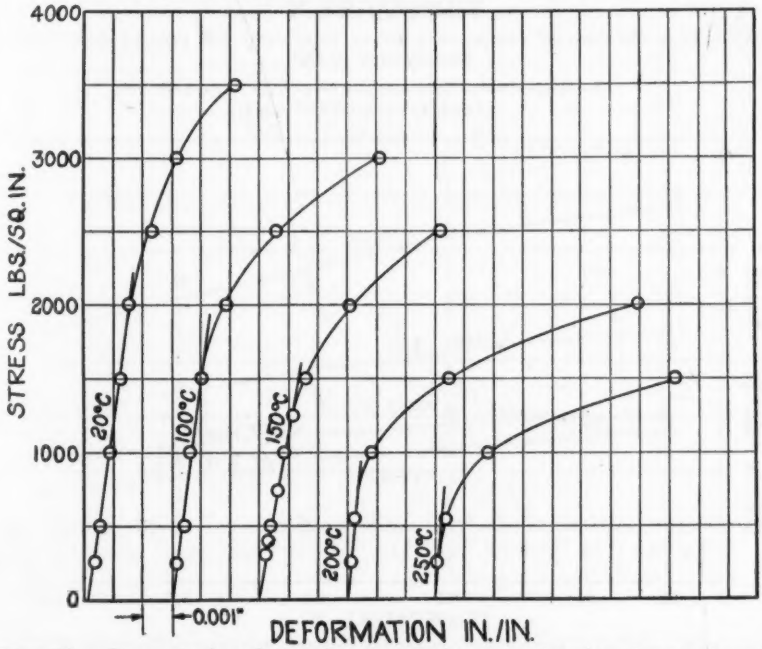


FIGURE 16.—*Stress-strain relation in compression tests at various temperatures for alloy B-14 (copper, 59.3 percent; lead, 40.3 percent and treated with 0.4 percent sulphur).*

Each plotted point represents an average of two determinations.

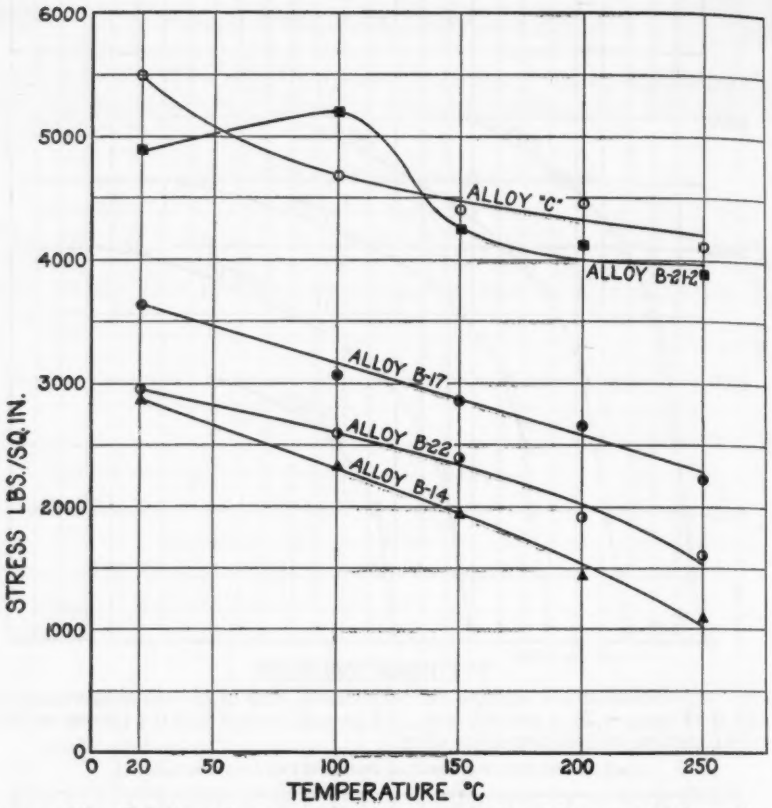


FIGURE 17.—*Relation of compressive stress producing 0.3 percent deformation to temperature of test.*

Each plotted point represents an average of two determinations.
Compositions given in Table 3.

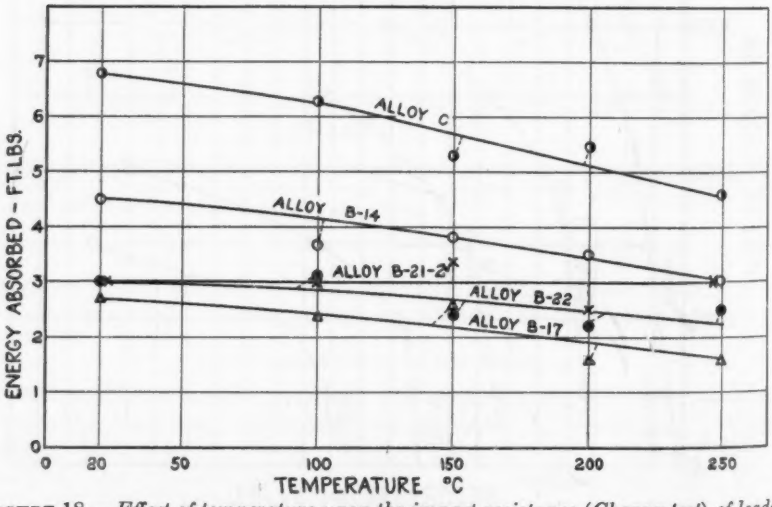


FIGURE 18.—*Effect of temperature upon the impact resistance (Charpy test) of leaded bronzes.*

Each plotted point represents an average of five determinations.
Compositions given in Table 3.

table 3. Alloy B-21-2 had considerably higher resistance to deformation at all temperatures than the other alloys and it is noteworthy

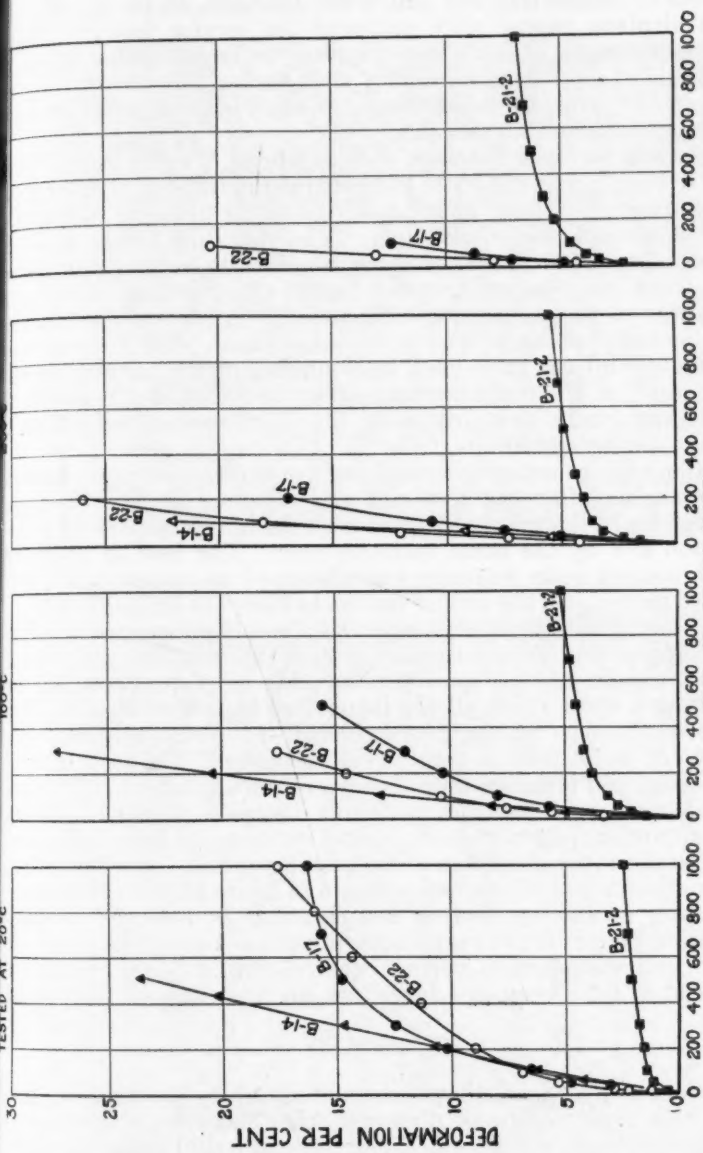


FIGURE 19.—*Pounding tests: relation at different temperatures of deformation to number of blows of hammer weighing 2 pounds and falling a distance of 2 inches.*

Each plotted point represents an average of two determinations. Energy absorbed by a specimen for each bowl of hammer was approximately 0.33 foot-pounds. Compositions given in Table 3.

that the rate of deformation of this alloy as shown in figure 19 was rather uniform from 100° to 250° C. (212° to 490° F.), inclusive.

IV. SERVICE TESTS

Two sets of connecting rod and main bearings, to fit the Wright type J-5 airplane engine were prepared for service tests.[15] These bearings were made of an alloy prepared to be the same as alloy B-21-2 (table 3), and were backed by steel shells. Chemical analysis of a sample of the bronze taken from a finished bearing indicated that the lead content was 33.5 percent.[16]

Service tests of these bearings were made at Wright Field. The bearings were run in a model V-1570 engine operated at 2,400 r.p.m. and developing 600 brake horsepower. The oil pressure was maintained at 75 pounds per square inch. The operating temperature of the oil was about 150° F. The engine appeared to be operating satisfactorily when No. 5 connecting rod broke, after running 68½ hours, due to failure of the connecting-rod bearing. A report from Wright Field indicated that there was a serious lack of bond between the bearing metal and the steel back in a number of the connecting-rod bearings and that the main bearings after the 68½ hours' run were in about the same condition ordinarily found in copper-lead bearings used under similar conditions.

A metallographic examination was made of several bearings removed from the engine after the test run and of some unused bearings, all of which had been prepared from material of practically identical composition and by the same manufacturer. The lead in both the used and unused main bearings was dispersed as rather small, well distributed particles in the copper matrix as shown in figure 20 (*a*). The structure of both the used and unused main bearings, made of an alloy of composition similar to alloy B-21-2 (table 3) was that which was characteristic of the specimens of this alloy prepared in the laboratory and upon which all the laboratory tests were made. This structure is the one which it is believed should be obtained and obviously can be secured in commercial bearings. The structures of the connecting-rod bearings were, however, quite different. The lead in several of these bearings was found to be segregated often as streaks, approximately perpendicular to the bearing face, and equal in length to the entire thickness of the bearing metal. The "streaky" or columnar structure of the lead is shown in figure 20 (*b*). The structure existing in the connecting rod bearings is believed to have resulted from factors in the manufacturing process which have not yet been sufficiently studied to perimt exact control. These conditions are believed to have been in a large measure the cause of the bearing failure.

V. SUMMARY

A series of copper-lead alloys, containing 35 to 50 percent lead together with small additions of several other elements, was prepared as pilot test castings. This was the preliminary step in an investigation having for its purpose the development of leaded bronzes of high lead content from which the tin and antimony ordinarily used as dis-

[15] See footnote 8, p. 597.
[16] Analysis made by J. A. Scherrer, Bureau of Standards.

FIGURE 20.—*Microstructures of cross sections of bronze linings of airplane main and connecting rod bearings made of leaded bronze similar to alloy B–21–2 (Table 3).*

The lead is represented by the dark areas. × 60. *A*, Main bearing. *B*, Connecting rod bearing.

UNIV. OF MICH.

persing and distributing agents for the lead were eliminated. The microstructures of these alloys were studied to determine the effect of the various additions on the dispersion and distribution of the lead particles throughout the copper-base matrix. The mechanical properties, such as resistance to wear, to impact (Charpy), to pounding (repeated impact), and strength in compression, which are believed to be of significance in the use of this type of alloy as bearings, were determined in comparison with those of similar commercially available alloys. Service tests were made on a set of connecting rod and main bearings for use in airplane engines. These bearings were prepared in a commercial plant from a leaded bronze containing about 35 percent lead, 0.4 percent sulphur, 1.5 percent silicon-zirconium alloy, and remainder copper, and developed during this study.

1. Individual additions of barium, calcium, zirconium, or sulphur to leaded bronzes showed promise in aiding in the prevention of segregation of the lead under the casting conditions used.

2. A leaded bronze free of both tin and antimony and containing sulphur and silicon-zirconium alloy was developed. The maximum lead content obtainable in this alloy was about 45 percent. The lead in the alloy was highly dispersed and uniformly distributed. Microstructural examination and mechanical tests indicated that the optimum additions to a high-lead bronze containing sulphur and silicon-zirconium alloy should be 0.4 percent sulphur and 1.5 percent silicon-zirconium alloy.

3. Laboratory wear tests on the sulphur-silicon-zirconium-treated leaded bronze and on a series of commercially available leaded bronzes of high lead content indicated that the wear resistance of the former was equal or superior to any of the commercial alloys tested, some of which contained up to 6 percent tin.

4. The results indicate that the compression strength of the new alloy, developed during this study, was as high as that of a commercial leaded bronze containing 10 percent less lead. This commercial alloy, however, showed higher impact resistance probably on account of the lower lead content, but the difference decreased materially as the temperature of test was increased.

5. The resistance to deformation under pounding for the leaded bronze, containing 0.4 percent sulphur and 1.5 percent silicon-zirconium alloy, was not materially affected by temperature, particularly between 100° to 250° C. (212° to 490° F.).

6. The structure and general physical appearance of bearings prepared of the sulphur-silicon-zirconium-treated leaded bronze for service tests indicate that this material can be readily handled commercially in the manufacture of bearings.

7. The main bearings removed from an airplane engine, which had been operated for 68½ hours, were in about the same condition as ordinarily found in copper-lead bearings used under the same conditions. Some of the connecting-rod bearings used in this engine failed. A metallographic examination of these bearings showed the lead to be segregated often as streaks equal in length to the entire thickness of the layer of bearing metal. These conditions are believed to have been in a large measure the cause of the bearing failures.

VI. ACKNOWLEDGMENTS

The authors are indebted to Louis Jordan, of this Bureau, for his suggestions and aid in the course of this investigation, and to J. B. Johnson, of Wright Field, War Department, through whose courtesy bearings for the service test were manufactured and tested and who also arranged for the furnishing of many of the Amsler wear specimens made of commercial leaded bronzes tested in the course of this investigation. Particular acknowledgment is made to Capt. W. H. Sadler, War Department, through whose efforts and interest on behalf of the War Department, this investigation was made possible.

WASHINGTON, February 1, 1933.

PURIFICATION OF HYDROCARBONS BY CRYSTALLIZATION FROM LIQUID METHANE. ISOLATION OF 2-METHYLHEPTANE FROM PETROLEUM[1]

By R. T. Leslie[2]

ABSTRACT

A method for purifying difficultly crystallizable hydrocarbons of low freezing points by crystallization from liquid methane has been developed. It consists in mixing the hydrocarbon with propane, ethane, ethylene, or other such low-boiling hydrocarbon and adding the mixture dropwise to liquefied methane. If a solid phase forms, it is separated from the liquid with the aid of a centrifuge and the volatile solvent recovered.

Apparatus for using the method on quantities up to approximately 100 ml has been devised.

A sample of 2-methylheptane was separated from petroleum, and its properties determined. It constitutes about 0.15 percent of the crude oil. The freezing point of 2-methylheptane is −111.3° C. Its infrared absorption spectrum was also obtained.

CONTENTS

	Page
I. Introduction	609
II. Development of the method	610
III. Apparatus for treating small quantities	610
IV. Construction of the centrifugal apparatus	611
V. Operation of the apparatus	613
VI. Isolation of 2-methylheptane from petroleum	615
VII. Properties of 2-methylheptane	616
VIII. Estimation of the 2-methylheptane content of crude petroleum	618
IX. Acknowledgments	618

I. INTRODUCTION

While crystallization is a valuable aid in the separation of hydrocarbons having boiling points which lie close together, many such hydrocarbon mixtures crystallize with difficulty or not at all. The absence of any strong tendency for the molecules to orient coupled with the high viscosity of the liquid suggest themselves as interfering factors. It should therefore be possible to encourage crystallization by the addition of substances which will produce a system of lower viscosity at low temperatures.

Such a problem was met in the separation of the constituents of petroleum from a fraction boiling between 115° and 120° C. This portion was found difficult to fractionate further by distillation, and cooling merely resulted in the formation of glasses below −100° C.

[1] Financial assistance has been received from the research fund of the American Petroleum Institute. This work is part of Project no. 6, The Separation, Identification, and Determination of the Constituents of Petroleum.

[2] Research associate representing the American Petroleum Institute.

Such a behavior is to be expected in view of the number of isomer octanes and naphthenes with boiling points this range. Few freezing points are reported f isomeric octanes which have been prepared sy thetically, probably partly because of this dif culty of crystallization.

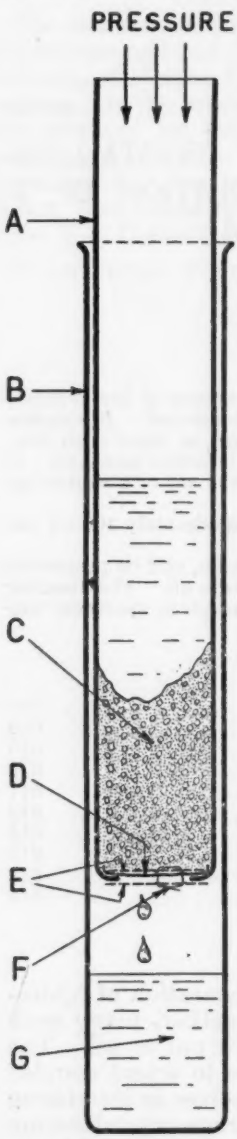


FIGURE 1.—*Apparatus for treating small quantities of material.*

A, filter tube; *B*, containing tube; *C*, solid phase; *D*, filter cloth or paper; *E*, perforated metal disks; *F*, wire holding plates together; *G*, liquid phase.

II. DEVELOPMENT OF THE METHOD

As diluents for these fractions, other hydr carbons with low boiling points meet most sati factorily the requirements of low viscosity very low temperatures and easy subsequent se aration. Dilution with propane at temperature below its boiling point (−45° C.) was first trie but was found to yield a mass on cooling belo −120° C. which, though apparently somewh crystalline in some cases, was too viscous fo manipulation. Ethane and ethylene were trie with similar results. Consideration of methan showed that its boiling point (−161° C.) wa below the congealing point of the fractions, an the addition of the petroleum fractions, whic had been cooled as far as possible without congea ing, to methane at temperatures below −161° C resulted in a stiff glassy material which showe no signs of crystallization or solution. In orde to get the fraction into solution in methane i was therefore mixed with sufficient ethane (belo −88° C.) to give a mixture of moderately low vis cosity at temperatures below the boiling point o methane. Addition of this mixture to methan resulted in the precipitation of a distinctly crys talline material, leaving a mobile liquid phas which was readily separable. While the mix ture of petroleum fraction and ethane yielde the more satisfactory precipitate, it was foun that ethylene or propane could also be used For the work described in this paper, commercia propane and methane condensed from natura gas were used.

III. APPARATUS FOR TREATING SMALL QUANTITIES

For treatment of quantities less than 50 ml the simple filter tube shown in figure 1 serve to separate the phases. Methane was poure or condensed into *B* to the depth of 5 or 6 cm with the filter tube *A* resting on the bottom of *B*. A precooled mixture of the hydrocarbon with approximately an equal volume of propane was made by cooling the hydrocarbon in solid carbon dioxide and condensing or pouring in the propane. This mixture was further cooled below the boiling point of methane and added to the

thane dropwise while stirring. It was found best to transfer the d liquids by forcing them by air pressure through vacuum-jacketed es in the manner in which liquid air is transferred. As soon as the thane reached saturation with respect to the least soluble constitu-, the solution became turbid and continued to thicken as more hydro-bon-propane mixture was added. The quantity which could be ded depended on the hardness and filterability of the precipitate. If lassy precipitate separated, it was found that the addition of more opane to the petroleum hydrocarbon sometimes improved the result. e liquid was filtered from the solid by raising the filter tube a few ntimeters from the bottom of the containing tube, as shown in the ure, and applying a gentle air pressure. After the liquid was blown m the filter tube, the latter was transferred to a second containing be similar to *B* which had been cooled to liquid-air temperature. th tubes were then connected to a condensing train and the low-iling hydrocarbons recovered by distillation. Most of the propane s caught in a solid-carbon-dioxide trap and the methane in a uid-air trap.

Caution must be observed in all the manipulations which have en described in which hydrocarbons are brought into proximity liquid air, especially in glass apparatus. Solid carbon dioxide pplemented by liquid nitrogen is advised whenever feasible. The esence of methane or propane in liquid air is readily detectable by e soapy appearance of the mixture. The high volatility of liquid ethane and propane should be kept in mind and free flames or parks should be avoided. Moving parts likely to become charged atically should be grounded. Care should also be taken not to low liquid methane to come into contact with the skin since it auses freezing much more rapidly than liquid air, apparently be-use of a wetting effect.

The natural gas which was used as a source of methane was trans-orted in light metal tanks having pressure gages attached. (Such anks are obtainable on the market as "gas sample tanks.") Larger anks, such as household hot-water reservoirs, were used for storage hile the smaller tanks were in shipment. The condensation of the ases from the reservoirs was carried out under a pressure of 50 or 0 pounds.

For the treatment of larger quantities of material the apparatus hown in figure 2 was used. It was essentially a basket centrifuge esigned to operate economically with regard to cooling agent at iquid-air temperatures and which was sufficiently gas-tight to permit ecovery of the volatile gases contained in it. The gases were rectified or subsequent use in the condensing train shown in figure 3.

IV. CONSTRUCTION OF THE CENTRIFUGAL APPARATUS

The centrifuge shell *I* of figure 2 was constructed of brass tube of such dimensions that it could be completely contained in a Pyrex dewar tube with about a quarter of an inch clearance. The apparatus used in this work was 7 cm in diameter at the top of the shell and 34 cm in height. Quantities of petroleum hydrocarbon up to 100 ml could be treated in it. The cover was constructed of bakelite and arranged for ready locking in position with the minimum of interfering projection either inside or outside the shell. The lower bakelite disk *J* had three projections which were slipped under cleats *H* of the

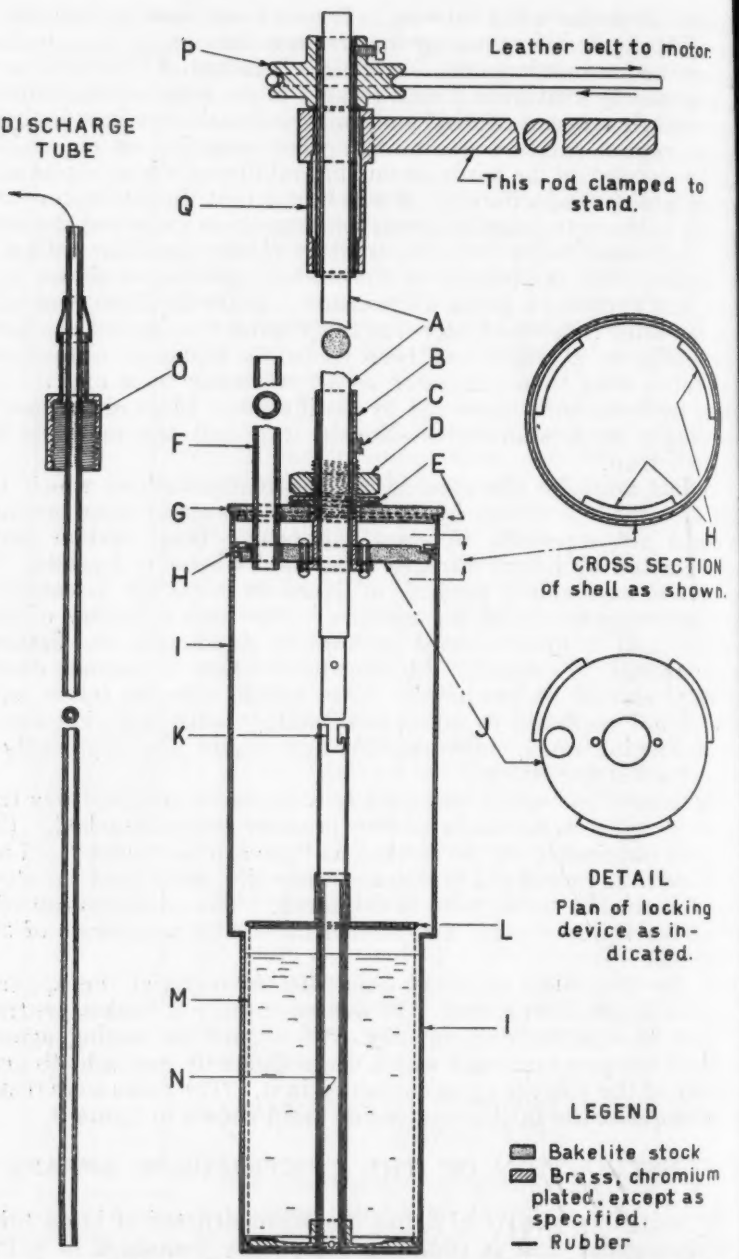


FIGURE 2.—*Centrifugal apparatus for separating solids and liquids at low temperatures.*

A, bakelite shaft; *B*, metal bearing; *C*, set screw for clamping basket in raised position; *D*, nut for drawing together two bakelite disks, *G* and *J*, to lock cover in position; *E*, rubber gaskets; *F*, bakelite vent tube tight in *G* but not attached to *J*; *G*, bakelite disk forming cover of centrifuge; *H*, brass cleats attached to shell and against which lower disk presses when cover is locked in position; *I*, shell of centrifuge; *J*, bakelite disk; *K*, bayonet lock for attaching shaft *A* to tube shaft of basket; *L*, removable metal cover of basket; *M*, centrifuge basket; *N*, bearing tube attached to bottom of shell *I* and having small holes in it flush with the bottom to admit liquid; *O*, brass cap for making discharge tube tight to *D* after removal of *A*; *P*, pulley for turning shaft; *Q*, metal bearing.

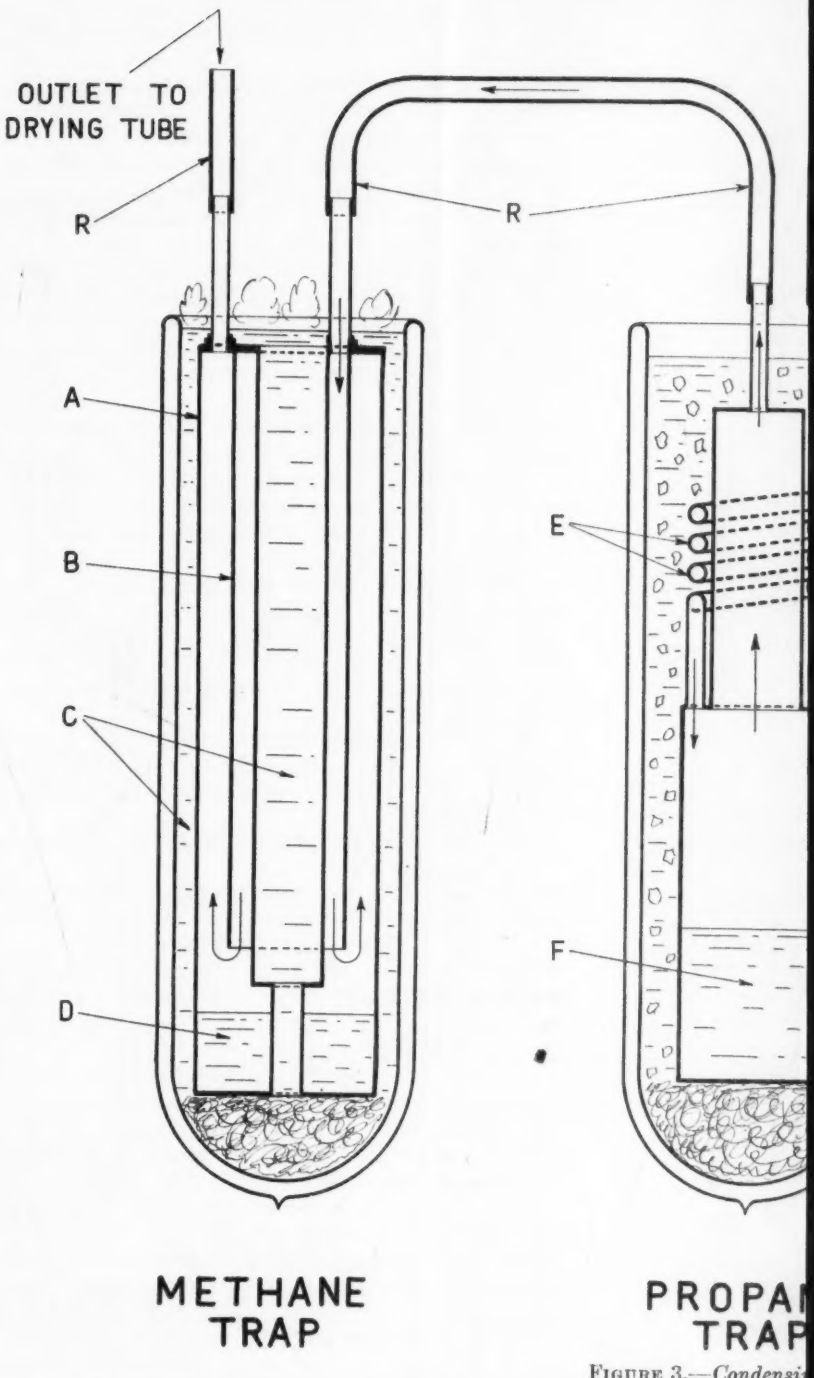


FIGURE 3.—*Condensi*

A, shell of methane trap; *B*, inlet skirt; *C*, liquid air; *D*, liquid methane; *E*, metal coils; *F*, liquid pr

167156—33. (Face p. 613.)

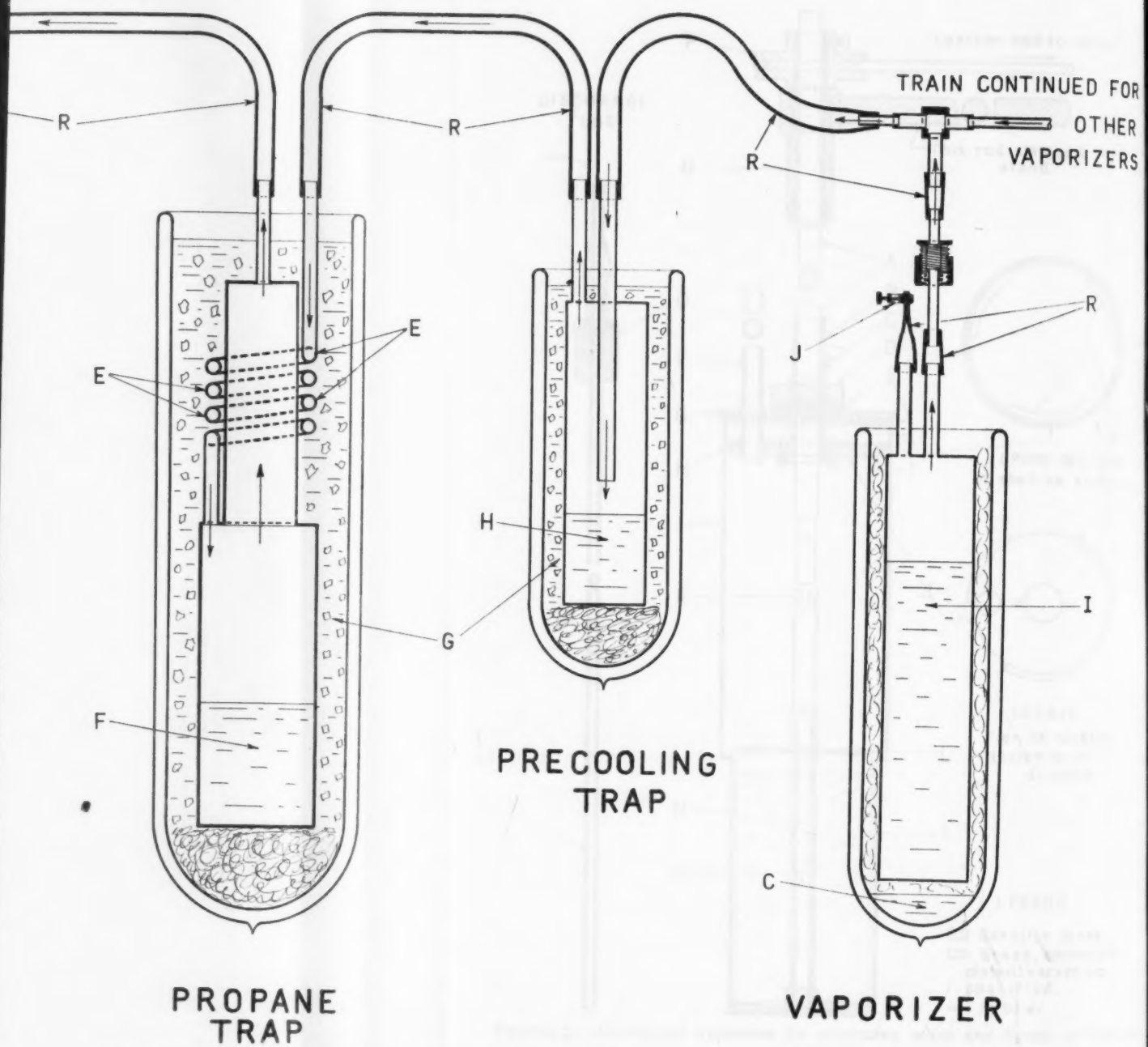


FIGURE 3.—*Condensing system for rectifying the low-boiling solvents.*

ir; *D*, liquid methane; *E*, metal coils; *F*, liquid propane; *G*, solid CO_2 in cryostat liquid; *H*, propane and ice; *I*, liquid fraction from centrifuge; *J*, pinchclamp; *R*, pressure tubing.

shell by a slight turn and the upper bakelite disk G was drawn down tightly against the top of the shell by the nut D.

The centrifuge basket was constructed of aluminum with perforated walls having about 700 holes per square inch. It was equipped with a removable top, L, to prevent splashing of the contents. It fitted snugly into the lower and smaller section of the centrifuge shell. The upper section of the shell was approximately 5 cm longer than the basket and had a diameter about 1 cm greater than that of the lower section. The tube shaft of the basket fitted over tube N below and into B at the top. Its upper end terminated in a bayonet lock, K, for attachment to the bakelite shaft. The small holes in N, which were bored flush with the bottom, allowed entrance of liquids into the shaft.

For recovery of the propane and methane so that they could be used again, the apparatus shown in figure 3 was employed. It consisted of a manifold to which small brass cylinders, of about 75 to 100 ml capacity, containing the samples could be attached, a simple trap for condensing moisture and propane, a second trap of more efficient construction for the removal of the propane from the methane as completely as possible, and finally a trap for the condensation of the methane. The first two traps were immersed in solid carbon dioxide and the third in liquid air. Several types of methane traps were used and the type shown was finally adopted because it showed the least tendency to become clogged by solid carbon dioxide, moisture, or hydrocarbon. Traps in which coiled tubes were used gave trouble from clogging though they were effective as condensers. The trap was of such capacity that enough methane could be collected in it to fill the lower section of the centrifuge.

V. OPERATION OF THE APPARATUS

The number of steps involved in the process makes it imperative to conserve time and energy if much material is to be treated. The operation will consequently be described in considerable detail.

The usual precaution in the matter of drying the apparatus before cooling should be observed to avoid clogging of tubes and sticking of moving parts. If the centrifuge is not dried between runs the basket is likely to freeze to the bottom. It can sometimes be loosened, however, when the propane and hydrocarbon mixture is added. To save liquid air, precooling was done as far as possible with solid carbon dioxide. Thus, the dewar tubes, the sample to be treated, the centrifuge cylinder, and the methane receiver were all cooled in this way before the addition of liquid air. The subsequent operations were usually performed in the order listed below:

1. Set up the condensing train as shown in figure 3, making sure that all outlets are closed, and allow the methane to condense under as much pressure as possible without causing the liquid air to spill. For condensing fresh methane the liquid air trap may, of course, be connected directly to the supply without intervening carbon dioxide traps.

2. Collect a volume of propane about equal to the volume of hydrocarbon to be treated and add it to the cold hydrocarbon.

3. Cool the centrifuge shell with liquid air and transfer to it the methane from the trap, as soon as the trap has been completely filled. Cessation of boiling of the liquid air is an indication of this, although

uncondensed gas sometimes collects in the trap and prevents furth entrance of methane. If the outlet of the trap is opened slightl the gas will escape; or if the trap is full, a small amount of liquid w be ejected.

4. Transfer the methane to the centrifuge as shown in position of figure 4. The methane trap should be opened carefully to t atmosphere before it is disconnected from the methane supply, sinc uncondensed gas sometimes collects in the trap and blows liqu methane out. Before attempting to pour the methane, the exit tub should be freed of frozen material by forcing a brass rod into it. T aid in directing the stream of methane, it is convenient to attach short bent glass tube to the exit tube. The inlet tube should b clamped shut during pouring.

5. Cool the mixture of propane and hydrocarbon to liquid air tem perature and force it slowly through a siphon into the methan which should be continuously stirred by means of a stirring rod, a shown in position I of figure 4. During this process the bakelite shaf should be in place in the central tube shaft of the centrifuge baske since methane is sometimes squirted from the tube by a percolato action. Addition should be stopped as soon as the mixture begin to thicken. The addition of too much material results in the forma tion of a mass which is too thick to centrifuge properly. It has bee observed that the fog which forms initially above the surface of th liquid frequently disappears when the precipitate begins to form As mentioned before, the formation of a glassy mass can sometime be prevented by enriching the added mixture with propane.

6. Assemble the centrifuge as shown in position II of figure 4 slide the precooled aluminum cover down the shaft to the baske lock the bakelite cover tightly in position, and mount for spinnin in some manner such as that indicated in figure 2. The cover aids i strengthening the basket but is not necessary. The basket should b raised to its spinning position slowly to prevent splashing or boilin of methane. The exit of the methane trap of the condensing syste should be opened to the atmosphere through a drying tube, and it i well to test the system for free passage by blowing into one of the inlet to the manifold before attaching it to the centrifuge. Stoppages occu in the small inlet tubes of the traps and can be opened by forcin a warm wire or rod into them.

7. The centrifuge must be rotated in such direction that the "bayo net lock" will remain fixed. Centrifuging should be begun slowly t avoid boiling the methane. It need not be very rapid (about 300 t 400 r.p.m.) and should be continued for a minute or two. It shoul be stopped slowly or the momentum may cause the basket to unloc from the shaft.

8. Demount the centrifuge and remove the liquid fraction, a shown in position III of figure 4. This is done by pulling up th basket as shown, so that the tube shaft projects into *B* (of fig. 2) where it is held by the screw *C* (of fig. 2) or by friction. The bakelit shaft can then be removed, leaving an opening to the bottom of th apparatus into which the siphon tube can be inserted. The sampl cylinders *V* must be cooled nearly to liquid air temperature and shoul be connected temporarily to the manifold of the condensing system b a rubber tube connection while the hydrocarbon is being forced int them.

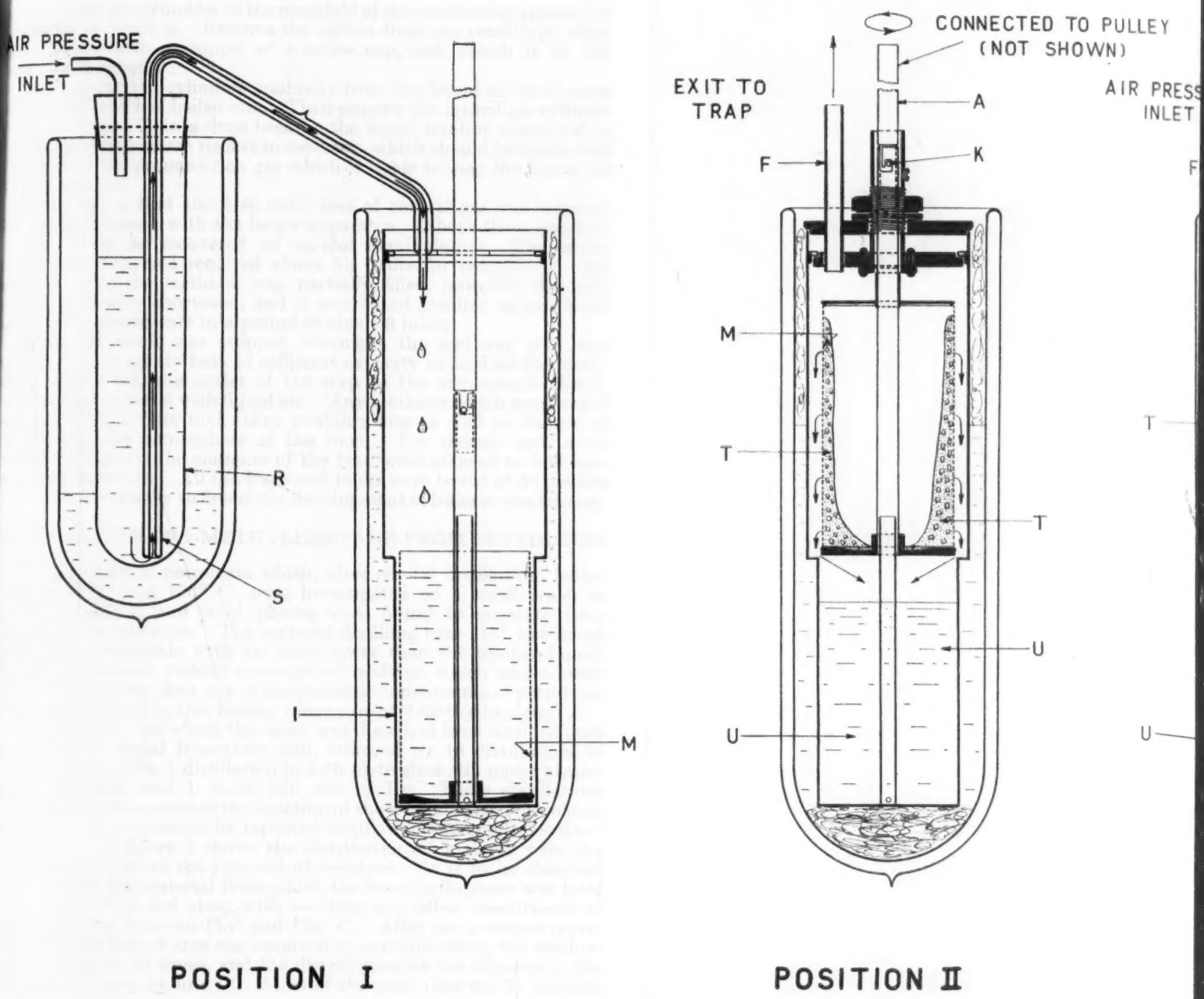
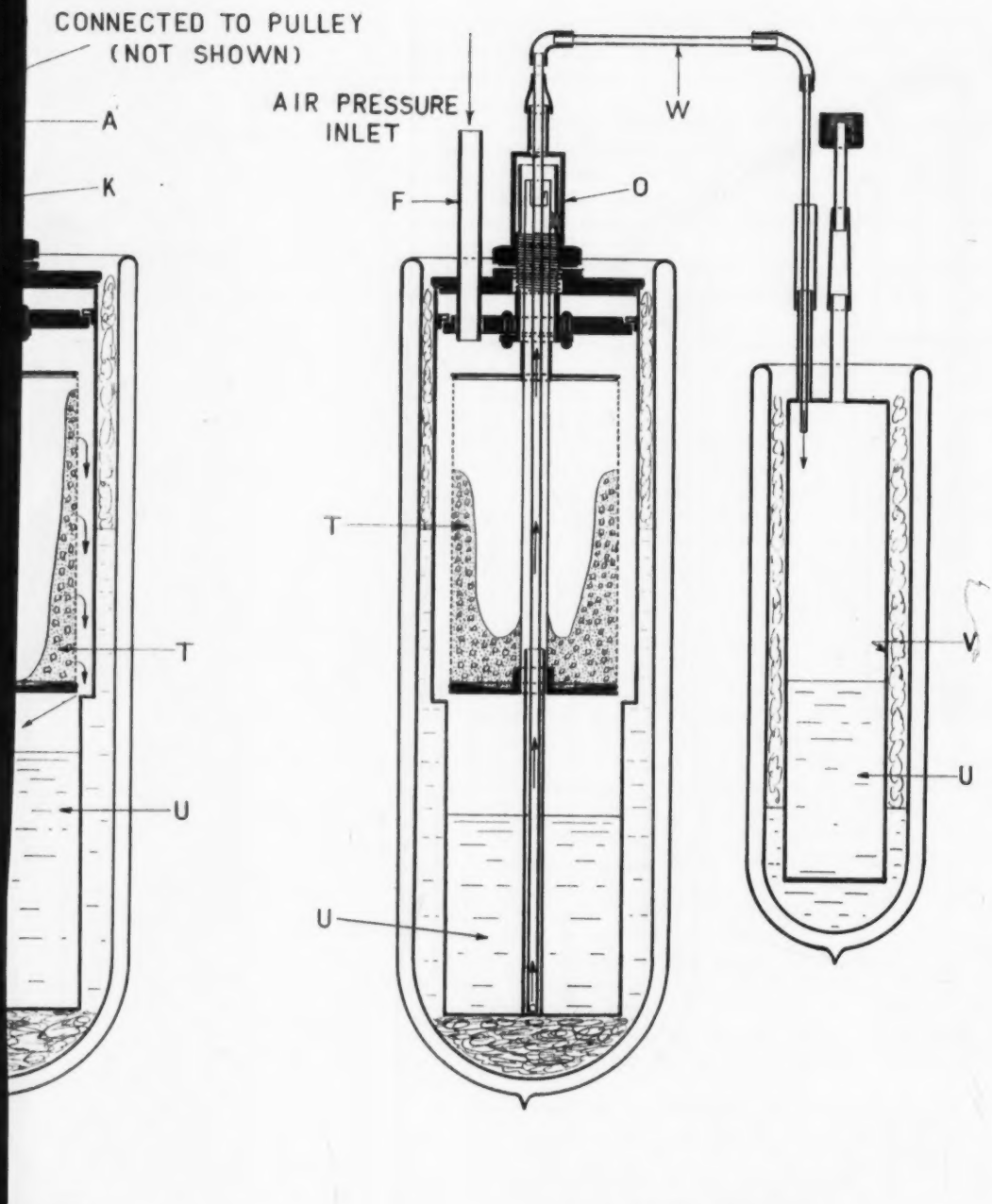


FIGURE 4.—*Operating positions of centrifugal separator.*

A, bakelite shaft; *F*, vent tube; *I*, centrifuge shell; *K*, bayonet lock; *M*, centrifuge basket; *O*, cap of siphon apparatus; *R*, glass test tube containing hydrocarbon-propane mixture; *S*, vacuum jacketed glass tube, as "vaporizer" in fig. 3); *W*, glass tube forming part of emptying siphon.



N II

POSITION III

ntrifugal separator.

n-propane mixture; *S*, vacuum jacketed glass tube; *T*, solid phase; *U*, liquid phase; *V*, brass tube for receiving liquid phase (shown art of emptying siphon.

167156—33. (Face p. 614.)

9. Attach the cylinders to the manifold of the condensing apparatus, as shown in figure 3. Remove the siphon from the centrifuge, close the opening with a stopper or a screw cap, and attach it to the manifold through *F*.

10. Remove the cylinders gradually from the liquid air until most of the methane has boiled out. Then remove the centrifuge cylinder from its tube. This is done because the liquid fraction contained in the small cylinders are richest in methane, which should be condensed first before the propane-rich gas which is liable to clog the liquid air trap is evolved.

It was found that about 50 cubic feet of natural gas was required for one experiment with the larger apparatus. About three quarters of this could be recovered by careful manipulation. The entire process as described required about 3½ hours for completion. By starting with the methane trap partially filled, however, the time was considerably shortened, and it was found possible to run three successive experiments in a period of about 8 hours.

When the work was stopped overnight the methane trap was attached to an empty tank of sufficient capacity to hold all the methane if necessary, the outlet of the trap to the atmosphere closed, and the trap covered with liquid air. Any methane which evaporated was received by the tank, thus avoiding loss as well as danger of escape into the atmosphere of the room. For storage over more prolonged periods the contents of the trap were allowed to boil into a storage reservoir. All the traps and tanks were tested at 60 pounds pressure occasionally to detect the development of leaks or weaknesses.

VI. ISOLATION OF 2-METHYLHEPTANE FROM PETROLEUM

The fractions of petroleum which, after careful distillation, boiled between 115° and 120° C. were investigated on a small scale, as described above, and solid phases were found to separate from several of the fractions. The material distilling near 116° was found to yield a precipitate with an index lower than the mother liquid. Further treatment yielded a sample of material which had a lower index of refraction than any of the probable constituents of petroleum likely to be found in this boiling range except 2-methylheptane.

The material [3] on which this work was done had been distilled once in a 20-plate metal laboratory still, followed by 10 distillations in 10-plate glass stills, 1 distillation in a 30-plate glass still under atmospheric pressure, and 1 under 726 mm of Hg. These distillations were made in the course of the isolation of the *n*-octane from petroleum as completely as possible by repeated distillation and crystallization.[4] Line No. 3 of figure 5 shows the distribution of material over the boiling range before the removal of *n*-octane. It is to be observed that most of the material from which the 2-methylheptane was later isolated was included along with *n*-octane and other constituents in the cut boiling between 118° and 128° C. After the *n*-octane represented by the dotted area was removed by crystallization, the residues were redistilled 10 times, and the distribution on the thirteenth distillation is shown by line 13. Most of the peak (line no. 3) between

[3] For description and properties of the petroleum, see Washburn, E. W., Bruun, J. H., and Hicks, M. M., B.S. Jour. Research, vol. 2, p. 469, table 1, 1929.

[4] All distillations were directed by S. T. Schicktanz, research associate representing the American Petroleum Institute.

118° and 128° was replaced by a somewhat narrower peak between 115° and 120°. The lower boiling material of this peak possessed a low refractive index approaching that of 2-methylheptane.

Beginning with the most promising fractions (those boiling at about 116° during the distillation or at about 117° in a Cottrell apparatus at atmospheric pressure) it was found possible to obtain filterable crystals from all of the material of the last distillation boiling between 115° and 117°. In all about 6.5 liters of material was treated by the process described, and 1,550 ml of material rich in 2-methylheptane was obtained. The average refractive index of the original material was 1.401^{20}, while that of the product was 1.3980^{20} and that of the residue 1.403^{20}. Redistillation of this residue yielded about 1,100 ml of material, which was treated a second time and yielded an additional 280 ml of product. This

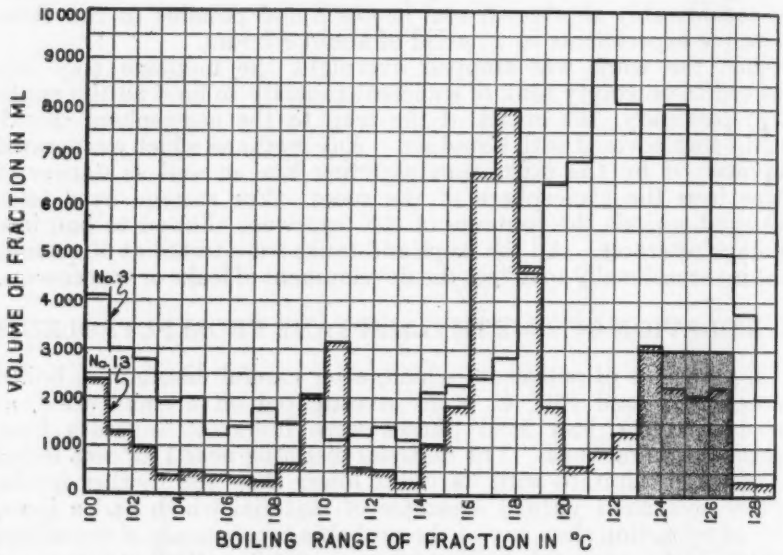


FIGURE 5.—*Graph of the distillation of the fractions of petroleum boiling between 100° and 129° C.*

product was sufficiently pure to show very definite arrests in the cooling curves, from which it was possible to estimate the quantity of pure material present. Because of the difficulty and expense involved, no attempt was made to purify the entire quantity of product.

VII. PROPERTIES OF 2-METHYLHEPTANE

In order to establish the identity and properties of the hydrocarbon isolated, 200 ml of "product" was given further successive treatments until the freezing point and refractive index ceased to change. This required six additional treatments, and 60 ml of purified material was obtained. Table 1 gives the observed properties of this sample (lot I), together with those of the other lots of product and the data for a synthetic sample reported in the literature. Figure 6 shows the melting and freezing curves of lot I. No data concerning

the freezing point were obtainable from the literature, and it will be observed that the refractive index of lot I is lower than that reported by Clarke, while its boiling point is higher. These discrepancies may probably be attributed to differences in the methods of measuring the properties, since the properties of the *n*-octane previously isolated from petroleum differ from those reported by the same author in the same directions and to approximately the same degree. The boiling points reported in the table were determined by means of a Cottrell boiling-point apparatus. The refractive indices were determined on a calibrated abbé split prism refractometer. The density was determined by pycnometers similar to the Ostwald-Sprengel type of about 20 ml capacity. A resistance thermometer previously described by Mair [5] was used for all freezing-point determinations.

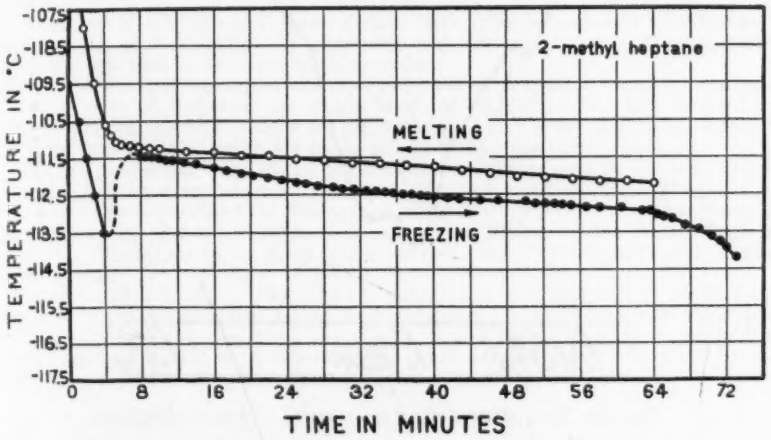


FIGURE 6.—*Melting and freezing curves of 2-methylheptane.*

This thermometer was calibrated in accordance with the specifications for the International Temperature Scale adopted in 1928.[6]

TABLE 1.—*Physical properties of 2-methylheptane*

Material	Normal boiling point	Freezing point (in dry air)	Refractive index n_D^{20}	Specific gravity	Purity	Volume
	°C.	°C.			*Mole percent*	*ml*
Synthetic [1]	116		1.3967	$0.7035\ ^{15}_{15}$		
Lot I	117.2	−111.3	1.3949	$.6985\ ^{20}_{20}$	97	60
Lot II	117.7	−117.0	1.3986		78	430
Lot III	117.5	−118.3	1.3985		73	420
Lot IV	117.5	−120.1	1.3995		67	470
Lot V	117.7	−116.6	1.3978		79	400

[1] Date reported by Latham Clarke, J.Am.Chem.Soc., vol. 31, p. 107, 1909.

[5] Mair, B. J., B.S. Jour. Research, vol. 9, p. 457, 1932.
[6] G. K. Burgess, B.S. Jour. Research, vol. 1, p. 635, 1928.

Since no data on the heat of fusion were obtainable, the molal lowering of the freezing point was determined by the addition of a known weight of toluene to the purest sample. This corresponded to a heat of fusion of approximately 2,200 g-cal/mol and from this the approximate purity of the other samples was calculated. The purity of the best sample (lot I) was estimated by assuming that the concentration of impurity in the solution had doubled at the midpoint of the freezing curve.

The infrared absorption spectrum as observed by U. Liddel, of the Fixed Nitrogen Laboratory, U.S. Department of Agriculture, is shown in figure 7.

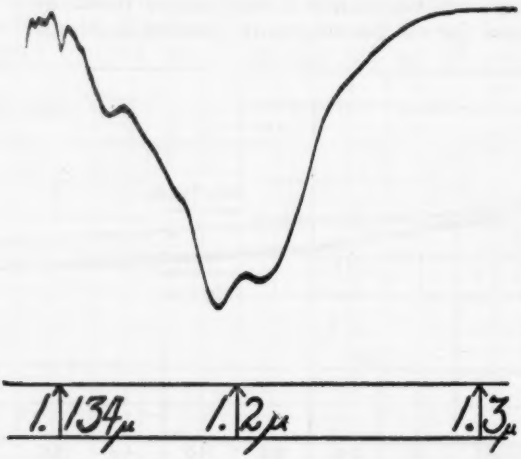


FIGURE 7.—*Infrared absorption curve of 2-methylheptane.*

The absorption band of iso-octane, composed of the second overtone frequencies of the fundamental carbon-hydrogen oscillation band around 3.4 μ. This is a portion of an automatically recorded energy-transmission curve through a 1 cm cell of iso-octane; the fine sharp absorption around 1.134 μ being due to atmospheric water vapor.

VIII. ESTIMATION OF THE 2-METHYLHEPTANE CONTENT OF CRUDE PETROLEUM

From the quantity of material isolated and an estimation of the losses incurred, it is concluded that the concentration of 2-methylheptane in the original curde oil was not less than 0.15 per cent.

IX. ACKNOWLEDGMENTS

The author acknowledges the technical advice of E. W. Washburn, Director of the American Petroleum Institute Project No. 6, and the assistance of J. D. White and F. W. Rose. He is also indebted to the Washington Gas Light Co. for supplying the natural gas from which the methane was obtained.

WASHINGTON, February 20, 1933.

THE EFFECT OF ALTITUDE ON THE LIMITS OF SAFE OPERATION OF GAS APPLIANCES[1]

By John H. Eiseman, Francis A. Smith, and Cecil J. Merritt[2]

ABSTRACT

The effects of altitude have been determined, from sea level to 11,000 feet, on the limits of safe operation of nine different gas appliances operated with a mixed city gas and in one case with propane.

It was found that the maximum safe gas rate, in B.t.u. per hour, is reduced by 3 to 4 per cent of the safe rate at sea level for each thousand feet of elevation. This reduction is about the same for all of the appliances tested with the exception of the radiant heaters which are more affected than the other types.

Data are presented from which preliminary estimates may be made of the size of the flue passages necessary at various altitudes for certain types of appliances. Other data show the effects of changes of altitude on the injection of primary air, the efficiency of the top burner of a range, the lifting of the flames from the ports, and the operation of pilot flames of both the "blue-flame" and "yellow-flame" types.

The effect of altitude in reducing the amount of gas that can be burned completely in a calorimeter was found to be the same with propane as with mixed city gas. It is concluded that the effects would have been the same had the comparison been made with other appliances or other gases.

Curves are presented which summarize the results quantitatively.

CONTENTS

		Page
I.	Introduction	619
II.	Equipment	620
III.	Appliances tested	621
IV.	Effect of altitude on the maximum safe gas rate	621
V.	Effect of altitude on the "blow-off" and "yellow-tip" limits	625
VI.	Effect of altitude on the area of flue opening required for a given gas rate	627
VII.	Effect of altitude on the total volume of the flue gases	631
VIII.	Effect of altitude on the injection of primary air	633
IX.	Effect of altitude on the efficiency of a top burner of a range	633
X.	Effect of altitude on the operation of pilot flames	634
XI.	Effects of altitude compared on two different gases	636
XII.	Summary and conclusions	637

I. INTRODUCTION

During the several years since the establishment of the Cleveland Testing Laboratory by the American Gas Association, there has been continual cooperation between the association and the Bureau of Standards in the matter of fundamental investigations. The results obtained in such investigations have been used to formulate standard methods for testing gas appliances, and minimum requirements which

[1] Presented in substance at the Washington meeting of the American Chemical Society, March 1933.
[2] Research Associate representing the American Gas Association.

various appliances should meet to insure safety and satisfactory service to the purchaser.

Largely as a matter of chance, the fundamental research which was necessary in order to draft approval requirements and also the routine testing of appliances to determine compliance with these requirements have been carried out at places which are not far above sea level.

The development of better methods of testing and the realization of the importance to the public of testing appliances have led to the establishment of various independent testing laboratories. Recently, one such laboratory, that of the Public Service Co. of Colorado in Denver, found that some of the appliances could not be operated with safety in Denver, at the gas rates for which they had been approved by the association's testing laboratory in Cleveland.

After a thorough checking of the results of both laboratories, the only reasonable explanation for such a failure of the standard test methods seemed to be the difference in the altitude of the two laboratories. Accordingly, the Bureau of Standards was asked to determine whether a change in altitude could account for the difficulties which had been encountered and to make a quantitative study of the effects on the limits of safe operation produced by changes of altitude. The Bureau was fortunate in having available an "altitude chamber" designed for the testing of aircraft motors which, with a few changes, was suitable for making appliance tests under substantially normal operating conditions at the barometric pressures corresponding to any desired altitude.

In order to make the results of this study generally applicable, and also to determine whether one type of appliance was more seriously affected than another, it was decided to test at least one representative approved model of each of the types of domestic gas appliances in most common use; namely, a water heater, a "circulating" space heater, a radiant heater, a range, and a central house-heating furnace. In all, eight appliances were tested with the mixed gas distributed in Washington. To these was added a manually operated gas calorimeter. The calorimeter was tested on the mixed gas and also with propane in order to determine whether the type of gas used affected the results.

II. EQUIPMENT

Figure 1 shows the interior of the altitude chamber, with a gas range installed for test. The chamber, which was approximately 8 by 8 by 18 feet, was supplied with compressed air, gas, water, vacuum, and electric connections. A large rotary exhauster provided means for reducing the pressure in the chamber, which, with the use of valves, could be held constant to 2 mm of mercury or less, this corresponding to less than 100 feet of altitude.

The instruments shown in figure 1 [3] were used to determine: (*a*) gas rate, (*b*) gas pressure at the appliance, (*c*) the constancy of composition of the gas supply, (*d*) the proportion of primary air in the mixture being burned, (*e*) the proportion of carbon dioxide in the flue gases, (*f*) the temperature of the flue gases, (*g*) the percentage of

[3] A Method for Determining the Most Favorable Design of Gas Burners, B.S.Jour. Research, vol. 8, p. 669 (RP446), 1932. Appendix describes the instruments for the determination of the data of items *c*, *d*, and *e*.

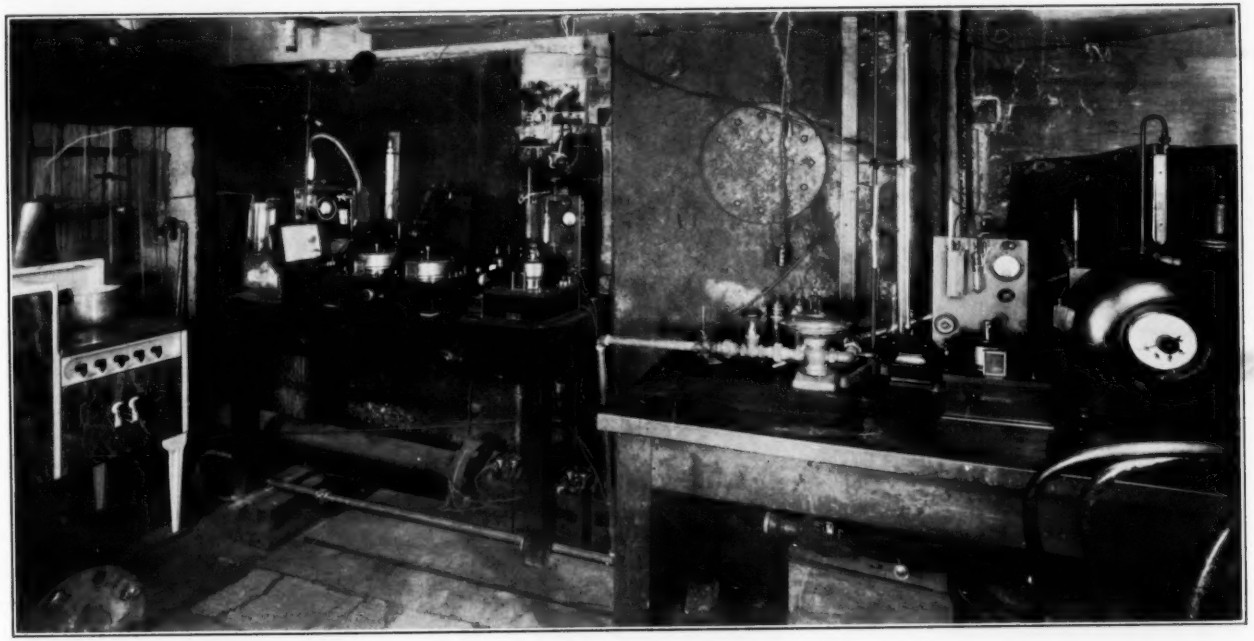


FIGURE 1.—*Interior of altitude chamber.*

carbon monoxide in the flue gases[4], (*h*) the temperature of the room, and (*i*) the barometric pressure, which throughout the paper will be expressed in terms of the altitude to which it corresponds.

In addition, provision was made for varying the area of the flue and for determining the efficiency of utilization of the heat from a top burner. A recording calorimeter located outside of the chamber made a continuous record of the heating value of the gas supply.

III. APPLIANCES TESTED

The following appliances were tested: Two "side-arm" water heaters—one of the copper-coil type *A* and the other having a cast-iron water jacket *B;* one gas range with a solid top *C;* one single-burner hot plate *D* supplied with an open grid; three space heaters—one of the circulator type *E* and two of the radiant type *F* and *G;* one gas-fired warm-air furnace *H;* and one manually operated calorimeter *I*. All of these appliances (with the exception of the calorimeter) had been tested and approved by the testing laboratory of the American Gas Association.

The variations in design, character, and size of these appliances were considered to be sufficiently great to make the results of the study of this group accurately indicative of what might be expected from any applianace in common use at this time.

IV. EFFECT OF ALTITUDE ON THE MAXIMUM SAFE GAS RATE

The method used for testing each of the appliances listed above was as follows: With the appliance installed in the altitude chamber in the usual manner and with the door of the chamber open (approximately sea level), the gas rate was adjusted to give the manufacturer's normal input rating measured in B.t.u. per hour. While the gas rate was held constant, the proportion of primary air to gas was varied from that which caused yellow-tipped flames to that which produced blowing or lifting of the flames. This variation was made in steps and the porportion of carbon monoxide and carbon dioxide in the flue gases determined at each step. The flue temperature and the relative proportions of primary air and gas were also recorded at each setting. By repeating this same procedure at several gas rates and plotting the primary air used against the carbon monoxide produced, it was possible to determine the amount of primary air which was required at each gas rate to give complete combustion.[5]

Backfiring was not a source of trouble with any of the appliances tested. There is every reason to believe that backfiring will occur less readily at a high than at a low elevation, hence this hazard was not studied.

The temperature of the flue gases was found to have very little relation to the altitude. It appeared to be almost entirely a function of the gas rate in B.t.u. per hour.

[4] The instrument for the determination of carbon monoxide was a continuous indicator recently developed by the Mine Safety Appliances Co. for the Navy Department.

[5] The range of gas rates was determined by the amount of primary air required for complete combustion. The lowest gas rate was the one which produced no carbon monoxide until the primary air was reduced to an amount which caused yellow tips, while the highest gas rate was the one which did not permit complete combustion when the primary air was increased to an amount just less than that which caused lifting of the flames. For a complete discussion of this method of testing and of representing the results, see Research Paper No. 446, referred to in footnote 3, p. 620.

Similar curves were obtained in the same manner at other altitudes by closing the door of the chamber and exhausting the air until the pressure in the room was the same as the normal barometric pressure at the desired altitude.

Figure 2 shows the effect of altitude on the operation of water heater *B*, the appliance which was studied in the most detail. The maximum gas rate that can be safely used is shown by the intersection of the "0 percent CO curve" with the blowing curve obtained at the desired altitude. For example, at an altitude of 200 feet, this intersection occurs at a gas rate of 26,600 B.t.u. per hour while, at an altitude of 10,900 feet, the intersection of the corresponding carbon monoxide and blowing curves occurs at 17,200 B.t.u. per hour.

The facilities available in the altitude chamber did not permit the lifting of the flames of some of the appliances to be readily observed

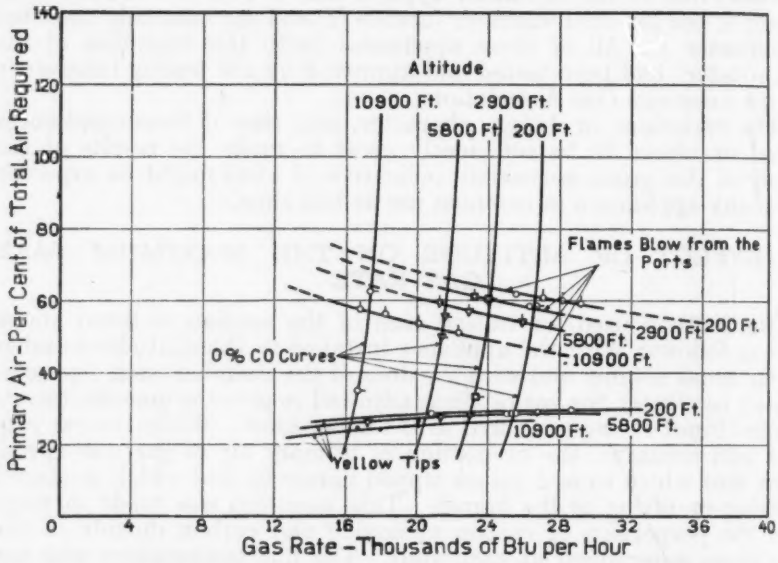


FIGURE 2.—*Effect of altitude on the limits of safe operation of water heater B.*

at their maximum safe gas rates. For this reason, as well as others, it seemed desirable to select, for comparisons between appliances, some basis other than the maximum safe rate. In the case of water heater *B*, it may be seen that the amount of air in the primary mixture which will permit gas to be burned safely at the maximum rate varies but little with altitude, from 61 percent of the total required at 200 feet to 57 percent at 10,900 feet. Most of the other appliances tested showed even narrower ranges of variation in the composition of the primary mixture which permits the use of a maximum amount of gas, and none of the five for which the necessary data were obtained showed a greater range. The range of uncertainty in the usual adjustment (by appearance) of appliances in use is considerably greater than this, hence no difference in the composition of the primary mixture supplied to appliances at various altitudes need be provided for by the designer or in the instructions to adjusters. There is no appreciable difference at different altitudes in the size or appearance of a flame produced by the same primary mixture burned

at the same rate in B.t.u. per hour. Differences of altitude may therefore be expected to have little or no effect on the average adjustment of appliances, with respect to either the gas rate or the composition of the primary mixture, if the appliances have been adjusted by appearance.

In view of these facts, it seems not only convenient but permissible to compare the operation of the same appliance at different altitudes when supplied with a primary mixture of the same composition, and similarly to base comparisons between different appliances on the same primary mixture. The mixture chosen for the purpose is one containing 55 percent of the "total air required" [6] for complete combustion and is probably near the average for which appliances are generally adjusted.

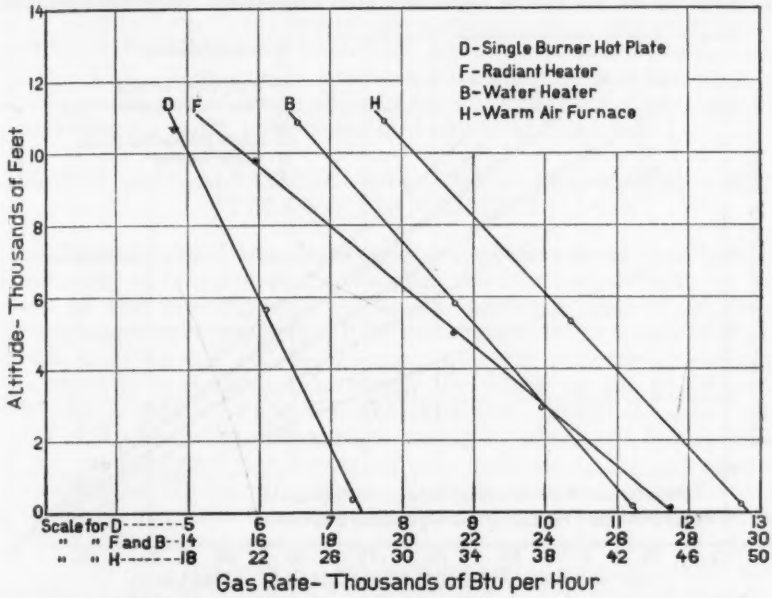


FIGURE 3.—*Straight-line relationship between altitude and the rate at which gas can be burned safely.*

The maximum gas rate which is safe at each altitude with 55 percent of the air required introduced as primary air is, of course, given by the intersection of the horizontal line representing 55 percent air and the "0 percent CO curve" for the same altitude.

These intersections for water heater *B* are replotted in figure 3, curve *B*, which shows that as the altitude is increased the maximum gas rate must be decreased if complete combustion is to be obtained. In terms of percentage, the maximum safe rate in B.t.u. per hour (at 55 percent primary air) which can be used at sea level is reduced 32.4

[6] By the "total air required" for complete combustion is meant the amount of air which contains enough oxygen to combine with all the constituents of the fuel to form water and carbon dioxide. Some of the appliances encountered had burners which were incapable of injecting 55 percent of this air at gas pressures up to 5 inches of water. In these cases it was necessary to provide means for forcing the primary air into the burner in order that the data from all the appliances might be compared on the same basis. Attention is called to the recommendation in Bureau of Standards Circular No. 394 of details of construction which will permit the injection of as much primary air as possible, any undesired excess to be controlled by means of a shutter.

percent when the appliance is operated with the same air adjustment at 10,000 feet.

Although the points plotted represent data only for primary mixtures containing 55 percent of the air required for complete combustion, corresponding data for other primary mixtures of constant composition showed substantially the same reduction in safe rate, as the altitude was increased.

From curves for each appliance similar to those shown in figure 3, the safe rates in B.t.u. per hour at various altitudes have been computed as percentages of the safe rate at sea level and plotted in figure 4. The safe rate for each individual appliance is represented by a solid line. The average of all appliances except the radiant heaters was practically coincident with the curve representing appliances I_o and D. This figure serves to indicate the variations between appliances

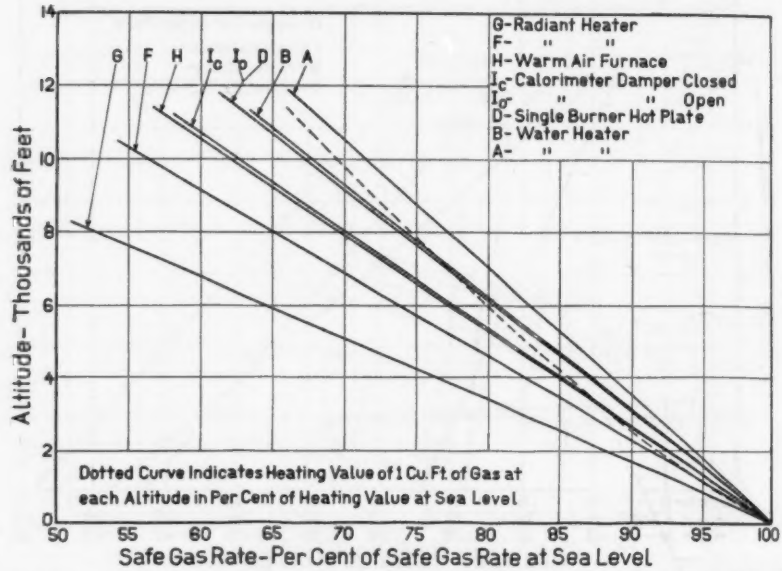

G-Radiant Heater
F- " "
H-Warm Air Furnace
I_C-Calorimeter Damper Closed
I_O- " " Open
D-Single Burner Hot Plate
B-Water Heater
A- " "
G F H I_C I_O D B A
Dotted Curve Indicates Heating Value of 1 Cu. Ft. of Gas at each Altitude in Per Cent of Heating Value at Sea Level
Altitude-Thousands of Feet
Safe Gas Rate-Per Cent of Safe Gas Rate at Sea Level
0 2 4 6 8 10 12 14
50 55 60 65 70 75 80 85 90 95 100

FIGURE 4.—*Effect of altitude on the safe gas rate compared on appliances differing greatly in design.*

of radically different mechanical construction, as well as the extent to which altitude affects the amount of gas that can be safely burned in a given appliance.

Curves D, F, and H of figure 3 represent observed limiting rates for other appliances at which it is possible to burn the gas completely when the primary air supplied is 55 percent of that required for complete combustion. In each case the maximum safe rate when plotted against altitude yields a straight line within the limits of accuracy of the observations. In view of the varied character of these appliances, it seemed safe to assume that linear relations between maximum safe gas rate and altitude would also hold for other appliances. Thus the necessity of testing at more than two altitudes could be avoided.

Referring again to figure 4, a reduction of 4.0 percent of the safe rate (in B.t.u. per hour) at sea level for every thousand feet of altitude appears adequate in practice to protect the user from the hazard of incomplete combustion in all cases except those of the radiant heaters.

The peculiar hazard of radiant heaters together with the fact that the heaters of this type which were tested showed very large and decidedly different reductions in the safe rate with change of altitude, indicates that a very liberal factor of safety should be chosen for these appliances. Certainly, the safe rate at sea level should be reduced at least 6 percent per thousand feet unless a smaller reduction has been found sufficient by actual trial.

The heat of combustion of a cubic foot of a given gas changes in proportion to pressure. For an elevation of 10,000 feet it decreases about 3.1 percent per thousand feet. The change which takes place with changing altitude is shown by the broken line (fig. 4). This reduction in B.t.u. per cubic foot is almost the same as the reduction in B.t.u. per hour required in the gas rate for the safe operation of most appliances except radiant heaters. It can, therefore, be readily seen that the average appliance will burn completely almost the same number of cubic feet per hour at one altitude as at another. This unexpectedly simple approximation can probably be used safely as a guide for the adjustment of appliances when they are known to have a fairly large margin of safety at sea level.

V. EFFECT OF ALTITUDE ON THE "BLOW-OFF" AND "YELLOW-TIP" LIMITS

In addition to the change in the position of the curves representing the beginning of incomplete combustion, the effect of altitude on the position of the blowing and yellow-tip curves is also of interest. Referring again to figure 2, it will be observed that for a constant gas rate both blowing and yellow tips occur at lower primary air settings as the altitude is increased, although the effect on the position of yellow tips is small. Figure 5, obtained from figure 2, shows the effect of altitude on the primary air setting at which the flames blew from the ports when water heater *B* was operated at the normal gas rate specified by the manufacturer. For this appliance the reduction of primary air required to avoid blowing at 10,000 feet amounted to 14 percent of the total air required. When we consider that the range of safe adjustment lies between the blowing and yellow tip curves and to the left of the "0 percent CO curve" (fig. 2) it is evident that the range of safe adjustment is greatly reduced at an altitude of 10,000 feet.

If, instead of comparing the amounts of air which cause lifting of the flames when gas is supplied at the same rate (in B.t.u. per hour) at various altitudes, the rates of flow of the same primary mixture are compared, a simple relation appears. It is found that lifting occurs with any given primary mixture at an altitude of 10,000 feet at about 56 percent of the rate in B.t.u. per hour at which lifting occurs at sea level and that if the ratio of the rate at each altitude to the rate at sea level is plotted against barometric pressure a straight line results. Average data obtained from several appliances are plotted in figure 6. This figure also shows that the volume of the primary mixture passing through the port when lifting occurs at 10,000 feet is about 82 percent of that passing at sea level. The data obtained with several appliances at several air-gas ratios agree within the probable limits of error of observation.

From this figure and a lifting curve obtained at one altitude it should be possible to construct with fair accuracy the lifting curve

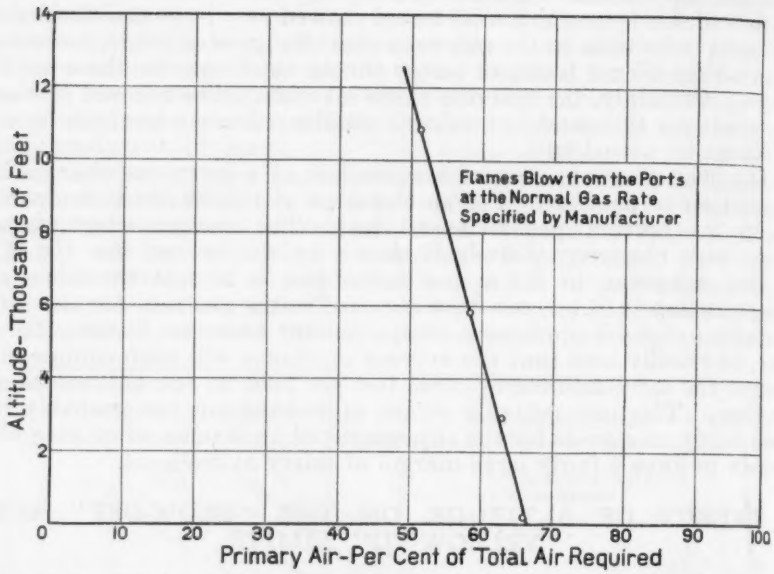


FIGURE 5.—*Effect of altitude on the primary air setting at which the flames blow from the ports.*

Water heater *B* operated at the normal gas rate specified by the manufacturer.

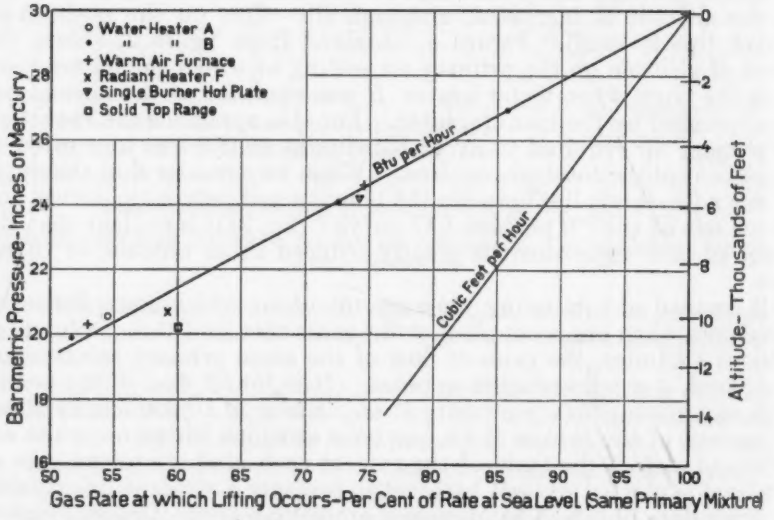


FIGURE 6.—*Effect of altitude on the gas rate at which lifting occurs with any given primary air setting.*

An average of five appliances.

for any other altitude, by making the indicated changes in the rate at which lifting occurs, for each of several primary mixtures.

VI. EFFECT OF ALTITUDE ON THE AREA OF FLUE OPENING REQUIRED FOR A GIVEN GAS RATE

It was apparent at the outset that a reduction of the barometric pressure from 29.92 inches at sea level to 20.58 inches at 10,000 feet would cause the volume occupied by 1 cubic foot of gas at sea level to be increased to 1.45 cubic feet at 10,000 feet. Similarly, the air required to burn this gas would have its volume increased in the same ratio, and so would the total volume of products of combustion and excess air which must escape through the flue opening.

The supply of secondary air to the appliance and the escape of products of combustion from it depend on convection through its open passages; hence, of course, the amount of secondary air available for combustion depends on the resistance to flow through such passages. In a rigorous consideration of the convection through an appliance the air inlets, combustion space, and flue passages would have to be considered as a whole; but in many appliances the resistance to flow is mainly determined by the minimum cross section of the passages, and frequently the point of minimum cross section is at the outlet or "flue collar." The expenditure of time necessary for a thorough study of the convection through appliances at various altitudes did not appear to be justified, but it did seem desirable to make observations of the effects which could be simply produced by changing the size of the flue outlet.

A double gate was provided, sliding at right angles to the axis of the flue pipe, by means of which the area of the flue opening could be varied continuously from wide open to closed.

In a typical experiment, the primary air was set at 55 percent of the total air required, with the appliance operating near to, and sometimes slightly in excess of, the maximum safe gas rate. The area of the flue opening was then decreased by steps, and the carbon monoxide, carbon dioxide, and the temperature in the flue gases were determined at each step.

By plotting the area of the flue opening against the carbon monoxide produced, it was possible to determine the area of the opening at which combustion became incomplete. In some cases this involved a small extrapolation to a flue area larger than the appliance possessed. This process was repeated at each of several lower gas rates and at each of several altitudes. Figure 7, obtained from tests of this nature on water heater *B*, shows a curve for each of four altitudes,[7] from which the area of flue opening required for complete combustion at various gas rates can be obtained for this particular appliance.

For example, at a gas rate of 16,000 B.t.u. per hour the smallest area of flue opening which will permit complete combustion at an altitude of 200 feet is 1.5 square inches. In order to burn gas at this same rate at an altitude of 10,900 feet an area of 4.25 square inches is required. The areas required at different altitudes have been obtained in this manner from figure 7, for each of several gas rates, and plotted as

[7] The curves have been drawn to intersect the horizontal line representing the "maximum" or unobstructed flue opening at points determined by the intersections, in figure 2, of the "0 percent CO curves" with the line representing 55 percent primary air. The observations by which these intersections were determined were entirely independent of and are believed to be more reliable than the observations which determined the other data represented in figure 7.

shown in figure 8. These curves show directly the effect of altitude upon the flue area required for complete combustion at any given gas rate. It is seen that, as the gas rate becomes higher, the area of flue

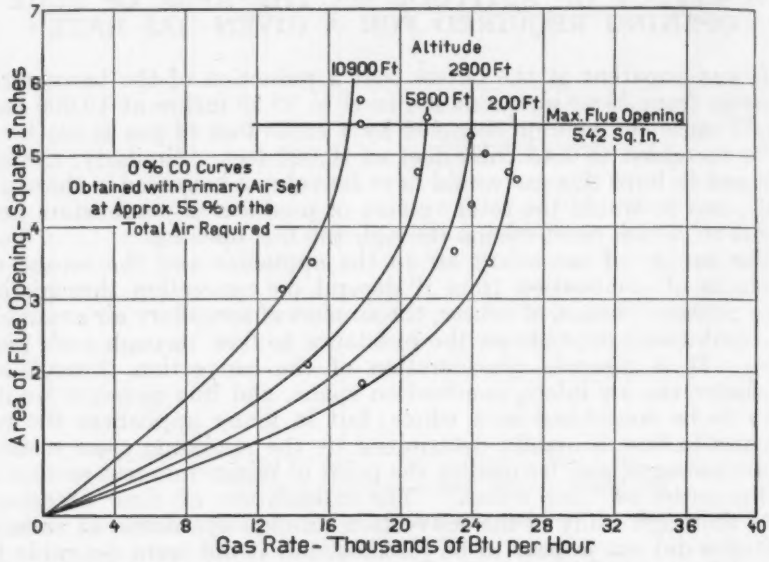


FIGURE 7.—*Effect of reducing the area of the flue opening of water heater B on the safe gas rate for various altitudes.*

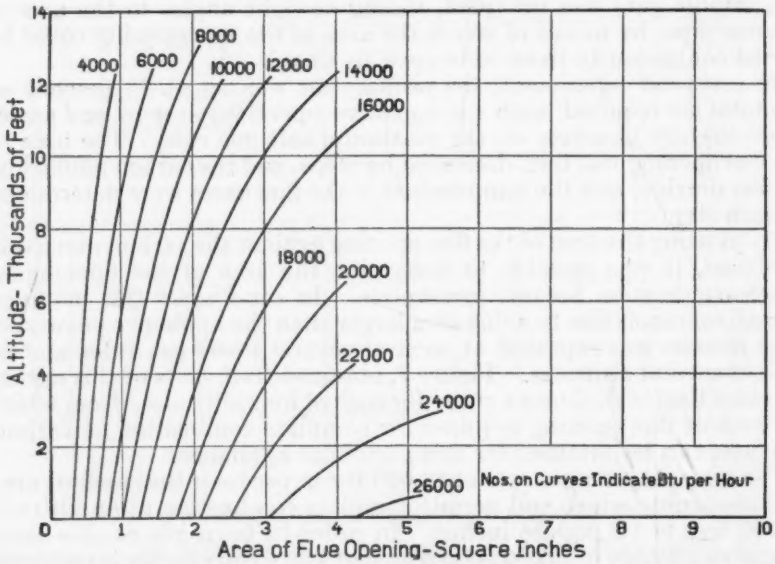


FIGURE 8.—*Effect of altitude on the area of flue opening of water heater B required for safe operation at various gas rates.*

opening required increases more and more rapidly with an increase in altitude. However, since each of the curves in figure 7 is approximately vertical at the maximum flue opening of 5.42 square inches, it is

evident that at no altitude would the safe capacity of this appliance be materially increased by enlarging the opening further. In other words, the safe capacity of this heater as it is built is limited by factors other than the area of the flue outlet.

Other appliances differ radically from this one with respect to the conditions which determine the relation between the area of the flue collar and the amount of gas that can be burned completely. The resistance to flow through the constriction at the flue collar may constitute almost the whole of the total resistance to flow through the appliance, or only a minor fraction of it. Incomplete combustion may result from the impingement of the flame on relatively cold surfaces under conditions which are nearly independent of the amount of excess secondary air. The secondary air may be so directed within the appliance that almost all of it, or only a part of it, comes into close contact with the flames and is thus available for supporting combustion. There are great differences in the height of the flue outlet above the burner and in the extent to which the products of combustion are cooled before reaching the outlet—factors that determine the draft "head" available to produce circulation. The problem is further complicated by the fact that many appliances have loose-fitting doors or other openings through which products of combustion escape to a certain extent when the vent is partially closed for purposes of study.

In spite of these differences, which might be expected to make impossible any useful generalization regarding the flueways of appliances, the data from five radically different appliances when plotted as in figure 8 gave series of curves so similar in character that, if not labeled, one set might readily be mistaken for any other.

When making quantitative comparisons between appliances of different sizes or types for the purpose of reaching general conclusions which may be of value to the designer, it is convenient to express the available data regarding the cross section of the flue in terms of square inches of flue area per 10,000 B.t.u. per hour, and the gas rate at which combustion becomes incomplete, as a percentage of the maximum safe rate, in B.t.u. per hour, at sea level. Curves plotted on this basis representing data from two appliances at two different altitudes and three other appliances near sea level are shown in figure 9. The curves representing water heater *B* are simply replotted on the new basis from figure 7, and those for the other appliances from corresponding curves representing their characteristics. It is again evident that the safe gas rate at high altitudes cannot be materially increased for either appliance *B* or *H* merely by enlarging the flue outlet; other parts of the appliance would have to be redesigned as well. From the curves representing conditions at approximately sea level it is apparent that the flue opening could be decreased without greatly affecting the maximum safe gas rate in the case of some but not all of the appliances. It is obvious that in no case, except possibly the warm-air furnace *H*, would further enlargement of the flue passages greatly increase the amount of gas that could be burned, unless other changes were made also. It is believed that the relatively large amount of gas that could be burned completely with very small flue outlets in appliances *A* and *E* was the result of leakage of flue gases through other openings.

For preliminary estimates by the designer of a water heater or other appliance in which all the secondary air passes close to a free-burning flame and the flue outlet is 2 feet or more above the level of

the burner, it appears that 2 square inches of flueway per 10,000 B.t.u. per hour of maximum demand at sea level should be a satisfactory figure. This does not mean that an appliance having this area of flueway will necessarily be free from the hazard of incomplete combustion; still less does it mean that it will be safe to obstruct the larger flue of an appliance already built. What it does mean is that if a designer uses a flue of the size computed from this factor and finds that the appliance does not burn the desired amount of gas completely at sea level, any considerable improvement is to be sought from changes in other details of construction rather than from an increase in the size of the flue outlet. If the flue outlet is near the level of the burner, or the products of combustion are greatly cooled before rising much above the burner, or if the flames are partially confined, or impinge on relatively cold solid surfaces, the factor given cannot be

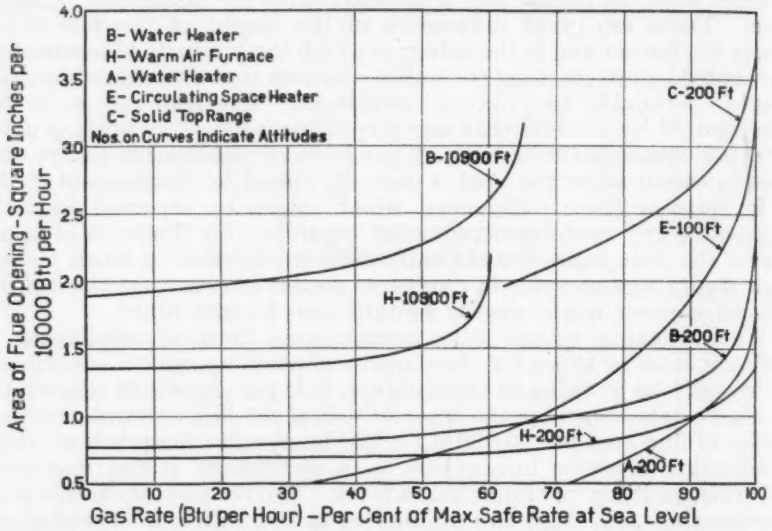


FIGURE 9.—*A comparison of the areas of flue opening required per 10,000 B.t.u. per hour for several appliances of different design.*

expected to apply, but one must be chosen which is appropriate to the type of construction employed.

To construct an appliance for use at a high altitude, it must be designed as a whole to burn at sea level an appropriately greater quantity of gas. An example will serve to make the method clear. Assume that a water heater is to be designed to have a "normal" rating of 25,000 B.t.u. per hour in Denver at an elevation of 5,280 feet. Since an increase in gas pressure (above atmospheric) of at least 50 percent above that at normal adjustment must be provided for (American Gas Association requirement), the appliance must be designed to burn gas where installed at a rate of at least $25{,}000 \times \sqrt{1.5} = 30{,}600$ B.t.u. per hour. Allowing for a reduction in the safe gas rate of 4 percent per thousand feet of elevation (see sec. IV), the maximum safe rate at 5,280 feet is 79 percent of the safe rate at sea level.

The safe rate at sea level which should be allowed for is therefore

$$\frac{30{,}600 \times 100}{79} = 38{,}800$$

The flue area to be chosen for preliminary use in design is then $3.88 \times 2 = 7.76$ square inches.

VII. EFFECT OF ALTITUDE ON THE TOTAL VOLUME OF FLUE GASES

In figure 10, curves are presented (from water heater *B*) showing the variation of the proportion of carbon dioxide in the flue gases with the gas rate, for each of four different altitudes, the primary air being held at 55 percent of the total air required.

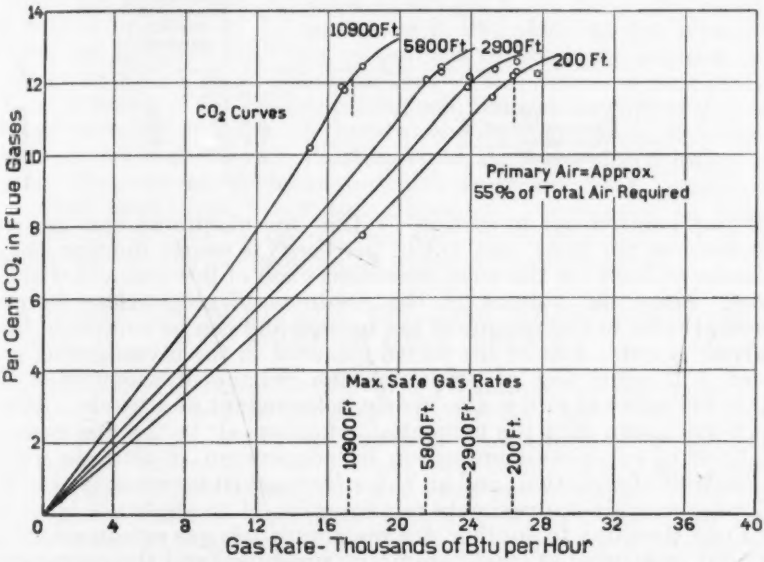


FIGURE 10.—*Relationship between the gas rate and the CO_2 content of the flue gases from water heater B at various altitudes.*

As can be seen from this figure, the concentration of carbon dioxide (at a given gas rate) increases as the altitude increases, or expressed in another way, a given concentration of carbon dioxide is obtained at a lower gas rate when operating at a higher altitude.

The broken lines in figure 10 indicate the gas rates above which carbon monoxide appeared in the products, for each of the four altitudes. When operating at an altitude of 200 feet, this gas rate is 26,400 B.t.u. per hour. Referring to the carbon dioxide curve for 200 feet, it is seen that at this gas rate the concentration of carbon dioxide was 12.1 percent. Similarly, at an altitude of 10,900 feet carbon monoxide appeared at a gas rate of 17,200 B.t.u. per hour, and the carbon dioxide concentration at this gas rate was also 12.1 percent. The same situation obtains at the other two altitudes.

Evidently, a carbon dioxide concentration of 12.1 percent is the highest obtainable with this appliance without incomplete combus-

tion, irrespective of the altitude at which the appliance operates. This corresponds to excess air to the extent of 15.0 percent of the total air required, which is unusually low.

Similar curves for other appliances indicate that when combustion became incomplete the excess air had been reduced to definite although somewhat higher values. Table 1 shows the excess air present when combustion became incomplete in the cases of the four appliances tested which were capable of yielding this information.

TABLE 1.—*Carbon dioxide and excess air at the maximum safe gas rate*

Appliance	CO_2	Excess air at maximum safe gas rate; average for various altitudes. Percent of total air required
	Percent	
Water heater *B*	12.1	15
Warm air furnace *H*	10.5	31
Water heater *A*	9.8	40
Circulator *E*	8.6	59

It was pointed out in section IV that the maximum safe gas rate in cubic feet per hour (not B.t.u. per hour) is nearly independent of altitude, at least for the most numerous class of flue-connected appliances. Since the volume of the products of combustion bears a constant ratio to the volume of gas burned and can be computed from analysis (1 cubic foot of the mixed gas used in the investigation produced 5.12 cubic feet of products), the volume of products at the maximum safe gas rate is also nearly independent of altitude. It has just been shown that the percentage of excess air in the flue gases at the limit of complete combustion is independent of altitude within the limit of observation, and all these facts taken together lead to the following roughly approximate relationship: If an appliance is moved from one elevation to another, the maximum safe gas rate in cubic feet per hour (measured at local barometric pressures) and the corresponding volumes of primary air, secondary air, products of combustion, and flue gases will remain approximately unchanged.

The rule is to be used only as an approximation. There are important departures from it which have been discussed in section IV.

A mental picture of what happens in the typical appliance may be had by considering the products of combustion as occupying an increasing proportion of the total capacity of the flue passages as the gas rate is increased, while the amount of secondary air which enters the appliance does not increase in proportion, and finally becomes insufficient to complete the combustion of the gas.

The constant excess of secondary air present in the flue gases in a given appliance when this condition is reached may be regarded as a measure of the efficiency of application of the secondary air.

VIII. EFFECT OF ALTITUDE ON THE INJECTION OF PRIMARY AIR

The top burner of a range was set to deliver approximately 9,000 B.t.u. per hour at 3½ inches pressure, and the primary air was adjusted to about 55 percent of the total air required, while operating at sea level. Leaving the orifice and air shutter as set, the altitude was changed to 10,400 feet, and the gas pressure reset at 3½ inches. The result was to change the gas rate from 8,970 B.t.u. per hour to 7,190 B.t.u. per hour, a decrease of 780 B.t.u. per hour. The percentage of primary air injected was not affected.

When the gas rate was restored to approximately 9,000 B.t.u. per hour (9,120), however, the gas pressure required rose to 5½ inches. The resulting effect on the composition of the primary mixture was again negligible.

When the orifice was adjusted to deliver 9,150 B.t.u. per hour at the normal pressure of 3½ inches, as it had done at sea level, the primary air injected fell from 54 percent to about 47 percent as it might be expected to do when the size of the orifice is increased.

The net result of the change of altitude, then, if the burner delivers the same number of B.t.u. per hour at the same gas pressure without a readjustment of the air shutter, is to decrease the primary air injected from 54 to 47 percent, which is of no great significance with most appliances, since the difference is not easy to detect from the appearance of the flames, and the original amount of air injected can usually be restored by opening the air shutter.

IX. EFFECT OF ALTITUDE ON THE EFFICIENCY OF A TOP BURNER OF A RANGE

The efficiency of a top burner of a gas range was determined in the manner described in Research Paper No. 446.[8] The burner was operated at sea level, and again at an altitude of 10,400 feet, at its normal rate of 9,000 B.t.u. per hour with the primary air set at approximately 55 percent of the total air required. Two efficiency determinations were made at sea level, two at 10,400 feet, and one more on returning to sea level. The results are presented in table 2.

TABLE 2.—*Effect of altitude on the efficiency of a top burner*

Test No.	Gas rate	Primary air, percent of total required	Altitude	Efficiency	Average
	B.t.u./hr.		*Feet*	*Percent*	*Percent*
1	9,120	53.8	0	31.2	
2	9,120	54.9	0	30.5	31.0
9	9,000	54.1	0	31.2	
7	9,150	53.6	10,400	33.2	33.2
8	9,090	53.2	10,400	33.1	

[8] See footnote 3, p. 620.

It appears that at the higher altitude the efficiency is slightly increased. This may be accounted for by a slightly better contact between flame and utensil at this particular distance between the burner and the utensil, which on this range was 2¼ inches. From considerations developed in Research Paper No. 446 [9] it is probable that the effect upon efficiency might be in either direction, depending upon the original adjustment of the burner. Variations in excess of 2 or 3 percent are not uncommon under normal operating conditions and, therefore, the variation obtained in this test cannot be assumed to be of much significance.

X. EFFECT OF ALTITUDE ON THE OPERATION OF PILOTS

Pilot flames may be divided into two general classes, those which are aerated (blue flame) and those which are unaerated (yellow flame).

A blue-flame pilot will be affected by altitude in exactly the same manner as the flame on any of the ports of the burner of an appliance and its behavior has therefore been covered by the foregoing discussion of the effects of altitude on the various characteristics of the main burners.

For example, the ratio of primary air to gas, in a blue-flame pilot of fixed mechanical construction, will be practically unaffected by altitude. It may also be assumed that the ratio does not change with the gas pressure (the fall of pressure through the orifice). The volume of gas delivered through a fixed orifice at a given gas pressure varies inversely as the square root of the density of the gas, and, of course, the volume of the primary mixture of constant composition varies in the same ratio. From these relations the relative volumes of primary mixture delivered at the same gas pressure at sea level and at any other altitude may be computed from the corresponding barometric pressures. From figure 6 the relative volumes of primary mixture which cause lifting at the two altitudes may be ascertained and by combining these facts with the well-known relation between the flow of gas and the fall of pressure through an orifice the relative gas pressures at which lifting will occur at the two altitudes may be easily found. A numerical example will make the method clear.

Assume that a blue-flame pilot is to be constructed, tested, and provided at sea level with a fixed orifice and primary air opening which will insure that it will be safe from lifting in Denver at a gas pressure of 15 inches. The case assumed to illustrate all the relations involved is an extreme one in that no adjustment whatever is provided for. The relative barometric pressures in Denver and at sea level are in the ratio of $\frac{24.6}{29.9}$ and the densities are in the inverse ratio. Hence, the volume of gas delivered through the fixed orifice in Denver will be

$$\sqrt{\frac{29.9}{24.6}}=1.10$$

times the volume delivered at sea level.

From figure 6 it is found that the flame will lift in Denver when the velocity of flow of the primary mixture is about 90 percent of that at

[9] See footnote 3, p. 620.

sea level. Hence, if lifting is to be avoided in Denver, the number of cubic feet per hour which the fixed orifice is to pass at sea level must not be greater than the fraction

$$\frac{0.90}{1.10}=0.82$$

or 82 percent of the rate which causes lifting at sea level. This limiting ratio may be arrived at experimentally by making use of the pressure relation. The rate at which gas is delivered through an orifice is proportional to the square root of the fall of pressure through the orifice, or stated in another way, the pressure is proportional to the square of the gas rate; hence, the flame must not blow from the port at sea level at a gas pressure less than

$$\frac{100}{82}\times\frac{100}{82}=1.5$$

times the pressure to be encountered in Denver, or a total of $15\times1.5=22.5$ inches.

To operate safely, a pilot must not only be safe from blowing off at the highest pressure likely to be encountered; it must also ignite the gas with certainty at the lowest pressure. It was observed that the length of a flame supplied with a primary mixture of given composition is dependent upon the total number of B.t.u. supplied and varies but little with altitude. Hence, to be safe at a high altitude, the pilot light should ignite the gas at sea level at the lowest rate in B.t.u. per hour likely to be delivered at the higher altitude. Since the volume of gas delivered at a definite gas pressure is inversely proportional to the square root of the barometric pressure, and the heating value per unit volume is directly proportional to the barometric pressure, the number of B.t.u. per hour delivered through a fixed orifice is proportional to the square root of the barometric pressure. Thus, in Denver, the number of B.t.u. per hour delivered through a fixed orifice is the fraction

$$\frac{24.6}{29.9}=0.908$$

or 90.8 percent of the heat delivered at sea level. To give the same rate in B.t.u. per hour the gas pressure at sea level must be the fraction

$$0.908\times0.908=0.833$$

or about 83 percent of that in Denver. If we assume that to be safe in Denver the pilot light must assure ignition at 1.5 inches pressure, it should cause ignition at sea level with 83 percent of 1.5 inches, or 1.25 inches pressure. Hence, to insure safety in Denver at all gas pressures between the extreme limits assumed, 1.5 and 15 inches, the pilot light should be tested at sea level between 1.25 and 22.5 inches.

A yellow-flame pilot burns gas with no admixture of primary air, and tests were necessary to determine the extent to which altitude would affect flames of several given heights burning on ports of different sizes. For these tests both the mixed gas of the city supply and propane were used.

The gas rate and corresponding height of flame were determined for two sizes of port (no. 66 and no. 48, drill manufacturers' standard) at sea level and at 9,900 feet, in one case with a flame about 2 inches high, and in another case at the gas rate at which the flame blew away from the port. The height of each flame was plotted against the gas rate, and all the points fell very close to a single straight line for flames up to 6 inches high. This indicates that, for all practical purposes, the height of an unaerated gas flame from a small opening such as is used for a pilot light is determined by the gas rate in B.t.u. per hour, regardless of altitude, size of port, or the kind of gas used.

The velocity of the gas stream was computed in the cases in which the flame blew away from the port. With a given gas and port size, the velocity required appeared to be independent of the altitude. With the mixed gas the velocity required was about the same for the two port sizes, but with propane it was slightly greater for the smaller port. The average velocity of the gas stream (both ports and both altitudes) required to blow the flames from the ports was 4.7 times as great for the mixed gas as for propane.

The flame which lifted most easily was that of propane, at the highest altitude, on the smallest port. It had a height of 6 inches, which is at least three times that needed for most pilots. This indicates that lifting from the port is not likely to be a source of difficulty at high altitudes any more than at sea level.

XI. EFFECTS OF ALTITUDE COMPARED ON TWO DIFFERENT GASES

In the case of the manually operated calorimeter, the primary air was set just high enough to eliminate yellow tips from the flame [10] and the maximum safe B.t.u. rate determined with the flue damper both in the open and in the closed position. This was done at sea level and at an altitude of 10,000 feet, using mixed gas and propane. Table 3 summarizes the results.

TABLE 3.—*A comparison of the effects of altitude with different gases*

Gas	Maximum safe gas rate (B.t.u. per hour)				Altitude, feet
	Damper open		Damper closed		
	Gas rate	Percent reduction per 1,000 feet	Gas rate	Percent reduction per 1,000 feet	
Mixed gas	8,400 5,625	3.29	5,060 3,175	3.73	0 10,000
Propane	8,400 5,600	3.33	4,975 3,025	3.90	0 10,000

The results indicate that the maximum safe gas rate, at a given altitude, with the damper open, was almost exactly the same with both gases.

[10] This is the primary air setting recommended for use with calorimeters of this type (see p. 66 B.S. Circular no. 48, Standard Methods of Gas Testing), and corresponds to about 30 percent of the total air required. In the case of propane the flame was slightly yellow, and the mixture contained about 25 percent of the total air required.

With the damper closed, the maximum safe gas rate at both altitudes was about 100 B.t.u. per hour less with propane than with mixed gas. The reduction of the maximum safe B.t.u. rate at sea level required for each thousand feet of altitude is also about the same for the two gases.

It therefore seems probable that the effect of changes of altitude with other appliances will not be very different for gases of different compositions.

XII. SUMMARY AND CONCLUSIONS

Nine gas appliances of distinctly different design were studied, and the effects of altitude on the limits of safe operation were found to be nearly the same for all of the appliances tested, with the exception of radiant heaters, which appeared to be more affected than other appliances. Excepting the radiant heaters, the maximum safe gas rate, in B.t.u. per hour, is reduced between 3 and 4 percent of the safe rate at sea level each thousand feet of elevation.

It is a simple but only roughly approximate general rule that an appliance, adjusted to take the same ratio of primary air to gas at two altitudes, can, without other adjustment, burn completely the same number of cubic feet of gas per hour at both altitudes. It will also receive the same volume of primary and of secondary air and will deliver the same volume of flue gases of the same composition at both altitudes. All of these volumes are as measured at the local barometric pressure at each altitude.

To construct an appliance for safe use at a high altitude, it must be designed as a whole to burn safely at sea level an appropriately greater quantity of gas. Some data are given from which preliminary estimates may be made of the necessary size of flue passages for certain types of appliances.

The effect of a change of altitude on the injection of primary air is not great enough to be detected from the appearance of the flames.

Unaerated or yellow-flame pilots are unaffected by changes in altitude, unless they are "smothered" by products of combustion from the main burner.

At the normal rate in B.t.u. per hour specified by the manufacturer, the percentage of primary air required to make the flames lift from the ports is reduced for each thousand feet of elevation by about 1.25 percent of the total air required. The rate at which a given mixture of gas and air can be delivered from a port without causing the flame to lift is reduced about 4.5 percent per thousand feet of altitude if rates are expressed in B.t.u. per hour, or about 1.75 percent if they are expressed in cubic feet per hour.

The effect of altitude on the efficiency of the top burner of a range was negligible.

The temperature of the flue gases has little relation to the altitude, but is almost entirely a function of the rate in B.t.u. per hour.

The effect of altitude in reducing the amount of gas that can be burned completely in a calorimeter was found to be the same with propane as with mixed city gas. It is concluded that the effects would have been the same had the comparison been made with other appliances or other gases.

WASHINGTON, January 28, 1933.

167156—33——5

ISOLATION OF ETHYLBENZENE FROM AN OKLAHOMA PETROLEUM [1]

By Joseph D. White [2] and F. W. Rose, Jr.[2]

ABSTRACT

Ethylbenzene having a purity of about 95 mole percent has been isolated from an Oklahoma petroleum. The density, refractive index, boiling point, and behavior on freezing of this sample have been determined and compared with the same properties of a very pure sample of synthetic ethylbenzene. A photograph of the infrared absorption spectrum of the ethylbenzene from petroleum has also been obtained. It is found that ethylbenzene constitutes about 0.03 of 1 percent of the crude petroleum.

The freezing points and composition of eutectic mixtures of ethylbenzene with meta- and para-xylene have been determined.

CONTENTS

	Page
I. Introduction	639
II. Methods and procedure	640
III. Properties of the isolated ethylbenzene	642
IV. Content of ethylbenzene in the crude oil	645
V. Acknowledgment	645

I. INTRODUCTION

With one exception, ethylbenzene has heretofore escaped detection by all investigators of the composition of petroleum. In a study of various petroleums (including a sample from Pennsylvania), Tausz [3] oxidized the distillation fractions boiling within a range which included the boiling point of ethylbenzene. From these he obtained, among other products, some benzoic acid which he assumed indicated the presence of ethylbenzene. Other workers, including Mabery,[4] have sought for ethylbenzene in vain.

This paper is an account of the isolation of ethylbenzene itself from an Oklahoma petroleum.[5] The separation of this hydrocarbon from the fraction in which it collected during distillation was accomplished by first extracting it, along with the xylenes, with liquid sulphur dioxide, and next subjecting the extract to a systematic crystallization and distillation. From the resulting ethylbenzene fraction, almost pure ethylbenzene was isolated by selective sulphonation and hydrolysis. Final purity was attained by repeating the sulphonation or by fractional crystallization.

[1] Financial assistance has been received from the research fund of the American Petroleum Institute. This work is part of Project No. 6, The Separation, Identification, and Determination of the Constituents of Petroleum.

[2] Research associate representing the American Petroleum Institute.

[3] Tausz, J., Zeit. angew. Chem., vol. 32 (I), p. 361, 1919.

[4] Mabery, C. F., Proc. Am. Acad. Arts Sci., vol. 31, p. 38, 1895.

[5] For description and properties of the oil see Washburn, E. W., Bruun, J. H., and Hicks, M. M., B.S. Jour. Research, vol. 2, p. 469, table 1, 1929.

II. METHODS AND PROCEDURE

The 45 liters of petroleum which distilled between 130° and 145° C. was extracted with liquid sulphur dioxide as previously described.[6] About 12 liters of extract was obtained, which consisted chiefly of a mixture of xylenes. Traces of aromatic hydrocarbons remaining in the immiscible or extracted fraction were finally removed with concentrated sulphuric acid.

Upon fractional crystallization of the extract, mother liquors from successive crystallizations were obtained which, while decreasing but slowly in refractive index, froze at surprisingly low temperatures; those from the final crystallizations froze far below the known freezing points of the xylene eutectics. This is to say, fractions accumulated which from their indices obviously contained aromatic hydrocarbons, but which from their freezing points obviously contained others in addition to the xylenes. When fractionation by crystallization was no longer feasible the mother liquors were further fractionated by extraction, alternated with distillation. This procedure yielded finally a fraction of 625 ml which boiled at 136° C., froze initially at −96° C. (with a second halt at −108° C.), and had a refractive index n_D^{25} of 1.480. These properties, as well as the odor, indicated that the material was impure ethylbenzene. At this stage of purification the major impurity was *m*-xylene. In order to remove most of this constituent, a sample of the fraction was sulphonated at 0° C. in the manner described elsewhere.[6]

The acid layer was separated from the unattacked oil and after dilution with an equal volume of water it was distilled with steam. This treatment resulted in the distillation of hydrocarbon as rapidly as it was liberated by hydrolysis from the sulphonic acid. The temperature of hydrolysis was regulated by boiling the acid solution when at the required concentration. The greater part of the recovered hydrocarbon was liberated thus at 130° to 135° C. This fraction was shown to consist almost entirely of *m*-xylene. However, a considerable portion collected when the temperature within the still was maintained at 155° to 157° C., the range (previously established) at which ethylbenzenesulphonic acid most readily hydrolyzes. Treatment of the remaining ethylbenzene stock in a similar manner yielded finally various fractions, the properties of which are listed in table 1.

TABLE 1.—*Fractions obtained by sulphonating the ethylbenzene stock at 0° C.*

Fraction	Volume	Temperature of hydrolysis	Refractive index n_D^{25} (uncorrected)	Initial freezing point (uncorrected)
	ml	*°C.*		*°C.*
Unattacked by H_2SO_4	375	----------	1.4755	−10[illegible]
m-xylene	125	130–135	1.4944 to 1.4941	−48.5 to −50.[illegible]
Intermediate	10	135–155	1.4941 to 1.4938	----------
Ethylbenzene	95	155–160	1.4931	−97.[illegible]

[6] White, J. D., and Rose, F. W., B.S.Jour. Research, vol. 9, pp. 714, 716, 1932.

The fraction obtained by hydrolysis at 155° to 160° C. was identified with greater certainty as ethylbenzene when a portion of it was oxidized with neutral potassium permanganate. Some carbon dioxide and a small amount (less than 5 percent) of isophthalic acid was formed, but the major part of the product was benzoic acid. This was considered to be confirmatory evidence for the presence of ethylbenzene.

The 375 ml fraction of oil left unattacked by sulphonation at 0° C. was now sulphonated at room temperature (about 30° C.) for 48 hours. An equal volume of acid was used and it was introduced dropwise with constant stirring. Treated in this manner, only 115 ml remained unattacked. Its properties indicated that it was probably a mixture of naphthenes and isononanes. It was combined with the main stock of petroleum distillate previously freed from aromatic hydrocarbons and is now in the process of analysis.

The acid layer (from sulphonation at room temperature), when diluted and distilled as before, yielded an additional 35 ml of impure *m*-xylene and 200 ml of ethylbenzene which was liberated at 146° to 158° C.

The various samples of ethylbenzene obtained by this hydrolysis ranged in freezing points from −97.3° to −99.6° C. as measured with a calibrated thermocouple of five junctions.[7] They were finally purified either by resulphonation and hydrolysis or by crystallization from a propane solution.

Resulphonation was carried out at room temperature. Upon hydrolysis, practically no oil was obtained within the range of temperature at which *m*-xylene is liberated, but nearly a third of the product of hydrolysis was released between 145° and 155° C. While this fraction consisted mainly of ethylbenzene, it nevertheless contained a considerable amount of *p*-xylene, as indicated by an initial halt in the cooling curve at a temperature well above the freezing point of ethylbenzene. This evidence of the presence of *p*-xylene was supported by the fact that its characteristic odor could be detected in the sample notwithstanding the pronounced odor of ethylbenzene. The refractive index of the sample, however, was higher by about 0.0001 than that for a sample of either *p*-xylene or ethylbenzene (which have nearly the same index). This would indicate that a small quantity of *m*-xylene was also present. The fraction was therefore rejected, and only the final two thirds of the product from hydrolysis was preserved. This was obtained between 155° and 160° C. and comprised about half of the sample the properties of which are given in table 2.

The presence of *p*-xylene in the fraction liberated by hydrolysis between 145° and 155° C. was anticipated from an experiment made to ascertain at what temperature *p*-xylene is regenerated by steam from its sulphonic acid. The results of the experiment showed that most of the *p*-xylene is obtained at a temperature between 145° and 147° C. Hence, it is to be observed that the ranges in temperature of hydrolysis of the sulphonic acids of *p*-xylene and ethylbenzene are

[7] These freezing points are doubtless too low by as much as a degree. At temperatures near its freezing point ethylbenzene becomes quite viscous and tends to supercool to a great extent before crystallizing. Forcing the supercooled sample to begin to freeze by immersing in it a rod chilled with liquid air causes a small amount of solid phase to form which is glassy in texture. Usually, several minutes elapse before the solid phase comes to equilibrium with the unfrozen liquid wetting the thermometer as shown by a constantly rising temperature. If along with supercooling the rate of cooling is rapid, as it was in the above cases, and the sample is impure, the initial freezing point cannot be obtained.

quite close together. With mixtures of the two, at least, these temperatures overlap. Furthermore, the two hydrocarbons react with sulphuric acid to about the same extent. Therefore, their separation from each other by sulphonation and hydrolysis is not sharp, and is at best fractional in nature.

Another portion of the ethylbenzene obtained from the initial sulphonation was purified by crystallization from a propane solution containing 3 parts by volume of the solvent to 1 of ethylbenzene. This solution was cooled to the temperature of liquid air in a centrifuge which could be operated at that temperature.[8] Crystallization took place and when a considerable amount of solid phase had appeared the mush was centrifuged at once. The crystals which were retained were partly melted and again centrifuged. Two thirds of the original sample was recovered in the crystal fraction. On cooling, this sample and the one from resulphonation behaved almost identically. Accordingly, the two samples were combined into one sufficiently large for careful measurements of its physical properties.

III. PROPERTIES OF THE ISOLATED ETHYLBENZENE

In table 2, the physical properties of the isolated ethylbenzene are compared with those of synthetic ethylbenzene reported in the literature. The table also shows a similar comparison made with a very pure sample of ethylbenzene obtained from the Bureau International des Étalons Physico-Chimiques in Brussels. The similarity in properties of the two samples serves well to identify the hydrocarbon isolated from petroleum.

TABLE 2.—*The physical constants of samples of ethylbenzene compared with previously reported constants for synthetic ethylbenzene*

Sample	Specific gravity d_4^{20}	Refractive index n_D^{25}	Normal boiling point	Melting point (in dry air)	Mole percent ethylbenzene
			° C.	° C.	
From petroleum	[1] 0.86679	[2] 1.49328	[3] 136.05	[4] −96.15	94.6
From Bureau des Étalons Phys.-Chim. (Timmermans)	[1] .86770	[2] 1.49336	[3] 136.28	−95.12	.....
Synthetic (previously reported)	[5] [6] .86690	[5] [6] 1.49317	[5] 136.15	[6] −94.4	.....

[1] ±0.00001. Determined by the Division of Weights and Measures of this Bureau.
[2] ±0.00005. Determined with a calibrated Abbé refractometer (Valentine design).
[3] ±0.05. Determined in a Cottrell boiler. The precision shown is for comparative purposes only.
[4] Temperature at which last of solid eutectic disappeared. (See fig. 1.)
[5] See Timmermans and Martin, J.chim.phys., vol. 23, pp. 733–759, 1926.
[6] Calculated from values given for 15° C.

As a test of purity of the isolated ethylbenzene, its behavior on freezing was determined. Its time-temperature cooling curve and melting curve [9] are shown in figure 1 as curve *II*.

Curve *I* in figure 1 shows the behavior on cooling of a solution containing 95 mole percent of pure ethylbenzene and 5 mole percent

[8] For description of the centrifuge see Leslie, R. T., B.S.Jour. Research, vol. 10 (RP 552), p. 611, 1933.
[9] These curves as well as others of a similar nature appearing in this report were determined with the 25 ohm platinum resistance thermometer used by Mair in his work on the physical constants of synthetic normal hydrocarbons. (See B.S.Jour. Research, vol. 9, p. 458, 1932.) The samples were cooled or warmed very slowly in a vacuum jacketed tube of 40 ml capacity and were forced to begin crystallizing when they were but slightly supercooled.

of pure *p*-xylene.[10] An initial break in the curve at −84° C. (not shown in the figure) indicated that *p*-xylene crystals first appeared at that temperature. The prolonged halt in cooling shown by the curve marks the freezing point (−95.88° C.) of the eutectic mixture of these two compounds. This mixture contains (as calculated from the lowering of the freezing point of ethylbenzene) 97.4 mole percent of ethylbenzene and 2.6 mole percent of *p*-xylene.

A similar cooling curve for a solution of 85 mole percent of ethylbenzene and 15 mole percent of *m*-xylene showed that ethylbenzene crystals first appeared at −100.05° C. and that the eutectic mixture froze at −101.05° C. From the lowering of the freezing point of ethylbenzene in this case, it was computed that ethylbenzene and *m*-xylene are present in the eutectic in the ratio of about 81 to 19 by weight.[11]

Comparison of the cooling curves shown in figure 1 revealed the fact that the sample of ethylbenzene from petroleum was impure.

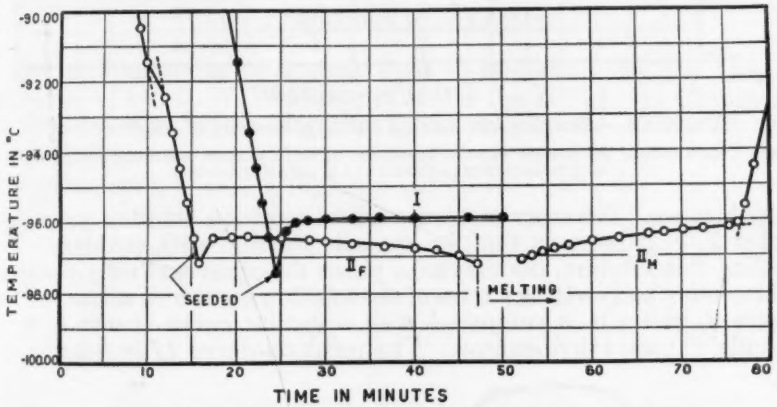


FIGURE 1.—*Comparison of the freezing and melting curves of ethylbenzene from petroleum with the freezing curve of a synthetic mixture of ethylbenzene and p-xylene.*

Curve *I*, synthetic mixture; curve *II*, ethylbenzene from petroleum.

That it contained only a minute amount of *m*-xylene was evidenced by the fact that its eutectic point at −96.15° C. was 5° above the eutectic point of *m*-xylene and ethylbenzene. The sample did contain, however, an appreciable amount of *p*-xylene as indicated by its initial freezing point near −92° C. and by the fact that its eutectic mixture froze but 0.27° C. below the eutectic point of pure ethylbenzene and *p*-xylene. The only conclusion that could be drawn from these data regarding the degree of purity of the sample was that it contained less than 96.5 mole percent of ethylbenzene (the eutectic

[10] The ethylbenzene used in this experiment was the best sold by the Eastman Kodak Co. It was purified further by selective sulphonation and hydrolysis and finally by distilling through an efficient column packed with jack chain. The properties of the sample used were:

$$d\,\frac{20}{4}=0.86746,\ n\,\frac{25}{D}=1.49327,\ B.P.=136.2°\text{ C.}\ M.P.=-95.15°\text{ C.}$$

The *p*-xylene used, and the *m*-xylene used in a later experiment were very pure samples obtained by us from petroleum. Their properties are listed in tables 3 and 4, B.S. Jour. Research, vol. 9, pp. 717, 718, 1932.

[11] The composition of this eutectic, as well as that for the *p*-xylene-ethylbenzene eutectic, was calculated by equation (47), p. 203, Washburn, Principles of Physical Chemistry, McGraw-Hill Book Co., 1921. For the heat of fusion of ethylbenzene the value of Parks and Huffman (Ind. Eng. Chem., vol. 23, p. 1138, 1931) was used. The difference in the molal heat capacities of its liquid and crystalline states was neglected.

composition) and probably more than 95 mole percent as judged by comparing its initial freezing point with that of a prepared solution containing that amount of ethylbenzene.

A more exact analysis was carried out in the following manner: Equal weights of the sample isolated from petroleum and of pure

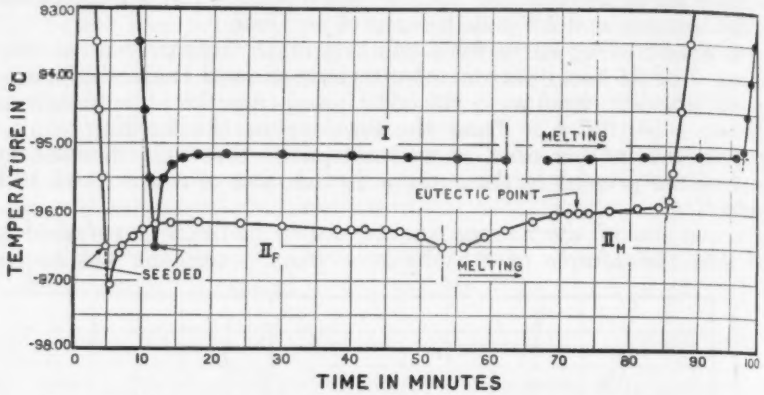


FIGURE 2.—*Freezing and melting curves of samples of ethylbenzene.*

Curve *I*, from Bureau des Étalons Physico-Chimiques; curve *II*, mixture containing equal weights of ethylbenzene from petroleum and of pure ethylbenzene.

ethylbenzene (Timmermans) were mixed to give a solution somewhat richer in ethylbenzene than its eutectic mixture with *p*-xylene. On cooling this solution, the first solid phase to appear was ethylbenzene. The cooling and melting curves of the solution are shown as curve *II* in figure 2, where it is compared with a similar curve (curve *I*) for a sample of pure ethylbenzene. The point on curve *II* indicating the

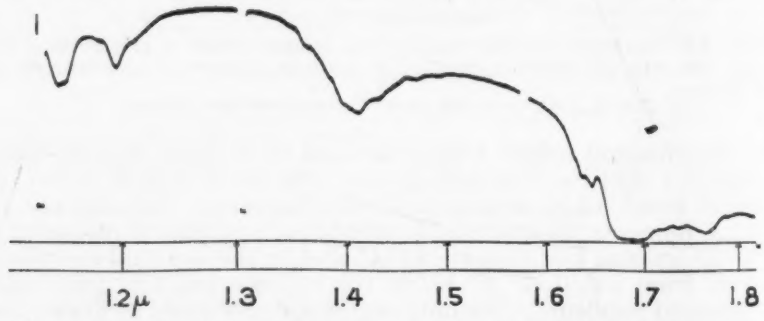


FIGURE 3.—*The infrared absorption spectrum of the isolated ethylbenzene.*

The spectrum, produced by ethylbenzene in a cell of 4 mm depth, is imposed on the energy emission curve of a tungsten filament lamp. Absorption in the region of 1.2 μ is due to the ethyl group and that near 1.14 μ is attributed to the aromatic nucleus.

temperature at which the second solid phase appeared is somewhat indistinct but is perceptible. This was to be expected in view of the fact that the freezing points of ethylbenzene and of its eutectic with *p*-xylene are so close together.

From the curves it was found that the impurity of the prepared solution caused the freezing point of ethylbenzene to be lowered by 0.78° C. It follows, then, by computation that this solution contained

97.3 mole percent of ethylbenzene and the original sample (which had twice the impurity) contained 94.6 mole percent of ethylbenzene.

Figure 3 shows the infra-red absorption spectrum of ethylbenzene isolated from petroleum. The photograph of the spectrum was obtained by U. Liddel, of the Fixed Nitrogen Laboratory of the U.S. Bureau of Chemistry and Soils.

IV. CONTENT OF ETHYLBENZENE IN THE CRUDE OIL

The total volume of ethylbenzene isolated from the fraction of petroleum amounted to nearly 300 ml. This, for the most part, was obtained from the distillation fraction boiling within the range of 130° to 136° C., and constitutes about 0.015 percent by weight of the crude oil. Allowing for losses of materials during the work, it is estimated that the content of ethylbenzene in the crude oil is more nearly, but not greater than, 0.03 percent by weight.

V. ACKNOWLEDGMENT

The authors desire to express their appreciation for the technical advice of Dr. E. W. Washburn, Chief of the Division of Chemistry at this Bureau, which they have followed in the course of this investigation.

WASHINGTON, March 9, 1933.

THE FLEXOMETER, AN INSTRUMENT FOR EVALUATING THE FLEXURAL PROPERTIES OF CLOTH AND SIMILAR MATERIALS

By Herbert F. Schiefer

ABSTRACT

An instrument is described with which the flexural work, flexural resilience, and flexural hysteresis of cloth, paper, sheet rubber, and similar materials can be evaluated. A pair of test specimens of standard dimensions are mounted in opposite angles formed by two vertical intersecting plates one of which is fixed and the other movable on a spindle. The work done in folding the specimens to various angles between the plates, the work recovered when they are allowed to unfold, and the work lost are measured. These quantities are a measure, respectively, of flexural work, flexural resilience, and flexural hysteresis of the specimens. They are related to the stiffness and creaseability of cloth and affect the sensations which contribute to the psychological qualities of "handle" or "feel" and the "drape" of fabrics. Typical results are given..

CONTENTS

	Page
I. Introduction	647
II. Flexometer	649
1. Description and test procedure	649
2. Calibrated springs	649
III. Illustrative data	651
IV. Discussion	654
V. Summary	657

I. INTRODUCTION

The "handle" or "feel" and the "drape" of fabrics are of great importance to the user of textiles in clothing and home furnishings, as well as to the textile designer and the textile finishing mill. They are psychological qualities and are commonly expressed only in the vaguest of terms.[1] Obviously the first step in the development of means for evaluating them is to provide adequate methods for evaluating the physical attributes of cloth that affect the sensations which contribute to "handle" and "drape." The purpose of this paper is to describe an instrument, the flexometer, for evaluating three of these attributes—flexural work, flexural resilience, and flexural hysteresis. Flexural work, flexural resilience, and flexural hysteresis are significant in other materials, such as paper, sheet rubber, patent leather, and varnish film. Typical results obtained with the flexometer for silk and cotton fabrics and for paper and sheet rubber are shown and discussed.

Other investigators have devised methods and instruments for measuring some physical characteristics of cloth that affect the sen-

[1] William D. Appel and the author are attempting to enumerate and define what may be called the kinaesthetic and tactile characteristics of cloth and the related physical properties.

sations which contribute to "handle" and "drape." Among the recent contributions may be mentioned a paper by Peirce on the handle of cloth as a measurable quantity.[2] Peirce measured thickness, weight, and the angle to which a specimen of definite dimensions droops under its own weight. He also discussed the relationship of these quantities to drape, feel, harshness, compactness, fullness, thinness, and paperiness. Peterson and Dantzig have developed a quantitative method for evaluating the stiffness of starched fabrics and have studied the effect of different starches.[3] McNicholas and Hedrick have described a method for measuring the resistance to bending and the elastic recovery under flexure of cloth and applied it to the evaluation of parachute cloth.[4] Mercier has published a method for determining the coefficient of friction of fabrics.[5] Schiefer has described a method for evaluating the thickness, compressibility, and compressional resilience of textiles.[6]

The general idea of the instrument to be described was suggested to the author by McNicholas as an improvement over the one described by McNicholas and Hedrick.[7] It is more sensitive than the instrument devised by Peterson and Dantzig and therefore can be used for delicate silk fabrics as well as for stiff cotton ones. Unlike the methods used by Peterson and Dantzig and by Peirce, the method to be described gives a measure of the amount of work done on the specimen in folding it through a definite angle. This value, the flexural work, is closely related to the stiffness of the specimen as appreciated by the fingers when the specimen is folded by them.[8]

The amount of work recovered when the specimen is allowed to unfold is also obtained. When expressed as a percentage of the work done in folding the specimen, this quantity is a measure of the flexural resilience of the specimen. So far as the author is aware, entirely satisfactory means of evaluating this characteristic have not previously been provided.

The difference between the work done in folding and the work recovered when the specimen is allowed to unfold—that is, the work lost—is partially expended in deforming or creasing the specimen. This amount of work when expressed as a percentage of the work done in folding the specimen, called flexural hysteresis, is closely related to the creaseability of the specimen. The angular crease in the specimen and the amount of work which must be done to bring the specimen back to its initial position, which are measured with the flexometer, are quantities also related to the creaseability of the specimen.

---

[2] F. T. Peirce, The Handle of Cloth as a Measurable Quantity. J. Textile Inst., vol. 21, p. 9, September 1930.

[3] E. C. Peterson and T. Dantzig, Stiffness in Fabrics Produced by Different Starches and Starch Mixtures, and a Quantitative Method for Evaluating Stiffness, U.S. Department of Agriculture, Tech. Bull. No. 108, 1929.

[4] H. J. McNicholas and A. F. Hedrick, The Structure and Properties of Parachute Cloths. National Advisory Committee for Aeronautics Tech. Note, No. 335, 33 pp., 1930.

[5] A. A. Mercier, Coefficient of Friction of Fabrics, B.S. Jour. Research, vol. 5 (RP 196), pp. 243-246, 1930.

[6] H. F. Schiefer, The Compressometer, An Instrument for Evaluating the Thickness, Compressibility and Compressional Resilience of Textiles, B.S. Jour. Research. (Will appear in June Journal.)

[7] See footnote 4. In their method a strip of fabric 3 by 9 inches in size is folded back upon itself and the height of the fold is measured when the fold is compressed by various loads. Similar measurements are made during unloading.

[8] Peirce assumed that the flexural rigidity, G, of the specimen is a measure of the stiffness as appreciated by the fingers. He computes it from the weight of the fabric per unit area, w, and from the angle, θ, to which a specimen of definite length, l, droops under its own weight, by the formula

$$G=\frac{wl^3\cos\theta/2}{8\tan\theta}$$

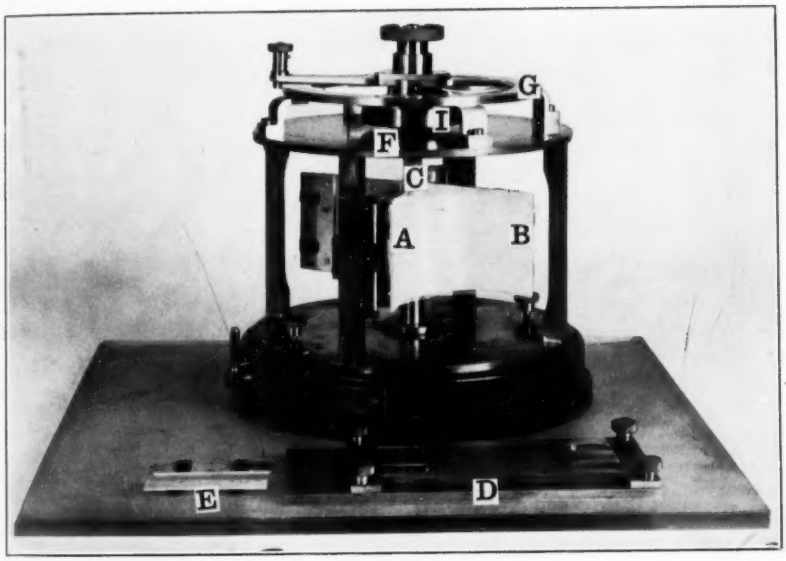


FIGURE 1.—*The flexometer.*

In this photograph the spiral spring was used to measure the torque. The spiral spring is mounted in the casing I.

II. FLEXOMETER [9]

1. DESCRIPTION AND TEST PROCEDURE

The flexometer with samples inserted ready for test is shown in figure 1. Two fixed plates, *A*, 2 inches wide and 2½ inches long, are attached to two diametrically opposite posts. A movable plate, *B*, 2 inches wide and 5⅝ inches long, is mounted on a spindle, *C*, which rotates freely on a small steel ball. The specimen to be tested, 1¾ inches wide and 6 inches long, is placed carefully in the mounting clamp *D*. The two small clamps, *E*, are given a thin coat of canadian balsam dissolved in benzol. They are then pressed against the specimen and stick to it. The excess material at each end of the specimen is cut off making the test specimen 4 inches long. The small clamps slip on the end of the fixed and movable plate as shown at *A* and *B*. The test specimen is tangent to each plate when mounted and will fold in the angle formed by the two plates when the angle between the plates is decreased by rotating the movable plate on the spindle.[10] As the specimen is folded between the plates, its resistance to folding or bending exerts a torque on the movable plate. For symmetry and to increase the torque exerted, a pair of specimens is tested simultaneously in opposite angles. The torque exerted by the specimens on the movable plate when they are folded to a certain angle between the plates is measured by the deflection of a calibrated spring which is attached to the spindle. The work done in folding the specimens through any small angle is given by the product of this small angle measured in radians and the average torque. If the torque is plotted against the angle between the plates, then the area under the curve bounded by any two angles is equal to the work done on the specimens in folding them from the larger to the smaller angle. The work recovered in unfolding is obtained in a similar manner.

2. CALIBRATED SPRINGS

Calibrated spiral or cantilever steel springs may be used with the instrument to measure the torque exerted on the movable plate by a pair of test specimens. Both types have been used and found to be satisfactory. If cantilever springs are used, then several springs of different capacities may be mounted permanently. With a set of six springs whose capacities bear a ratio of 1 to 2, specimens whose resistance to bending vary in a ratio of 1 to 32 may be tested by merely changing a spring-deflecting pin from one deflecting spoke to another. The springs are conveniently fastened to a hub at the top of the movable plate at an angular spacing of 60°. Another hub with six spokes is fastened to a knob at the top. By placing the deflecting pin in any spoke at a constant distance from the center, the spring directly below it may be deflected. The angle through which the spring hub or movable plate is rotated is indicated by a pointer, *F*, on a scale graduated in degrees. The spring deflection is obtained from the reading of a second pointer, *G*, on a similar scale.

In figure 2 is shown a typical calibration curve for one of the cantilever springs. The spring deflection in degrees is plotted as abscissa

[9] William D. Appel gave a brief description of the flexometer before Committee D-13, American Society for Testing Materials, on Mar. 13, 1930. This was published in Textile World, vol. 77, no. 13, p. 61, Mar. 29, 1930.

[10] For paper and starched fabric the specimens may be mounted so that they will fold outside of the angle formed by the plates. This should be done whenever no crease or set is desired in the specimens.

and the torque in ergs per degree is plotted as ordinate. The combined friction in the spindle bearings of the movable plate, in the

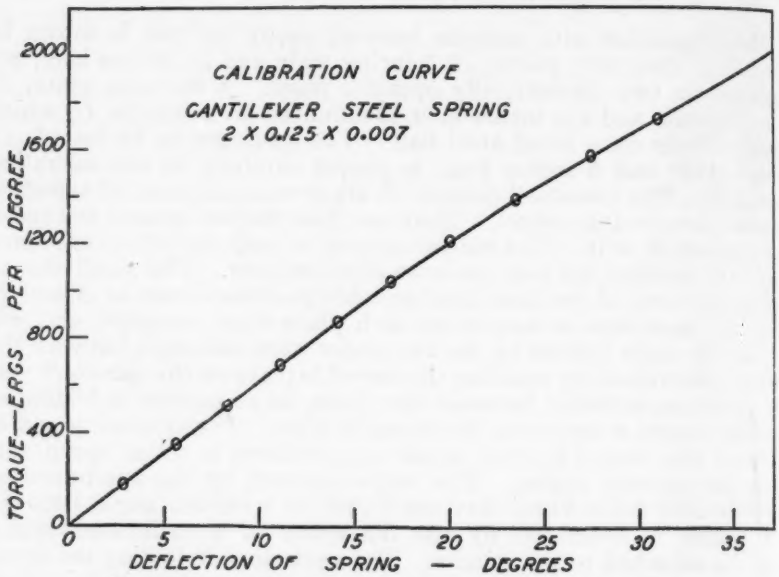


FIGURE 2.—*Calibration curve of a cantilever steel spring.*

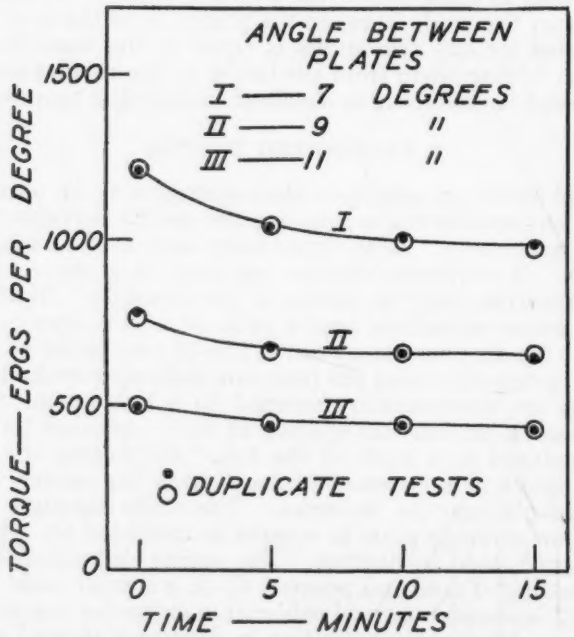


FIGURE 3.—*Curves showing effect of time and angle between plates on the torque developed by pairs of test specimens of a silk fabric.*

bearings of the calibration pulleys, and at the contact of the deflecting pin and spring amounts to approximately 3 percent of the torque at

maximum spring deflection. The effect of friction was eliminated in the tests by the method adopted for testing.

The calibration curve for a spiral spring is similar to that of a cantilever spring. However, for a given torque the deflection of a spiral spring may be 10 to 20 times that of a cantilever spring.

If many specimens are tested with one spring, then a calibration table will facilitate the computations greatly and save much time.

III. ILLUSTRATIVE DATA

In figures 3, 4, and 5 are shown typical curves obtained with the flexometer for different materials and under different methods of

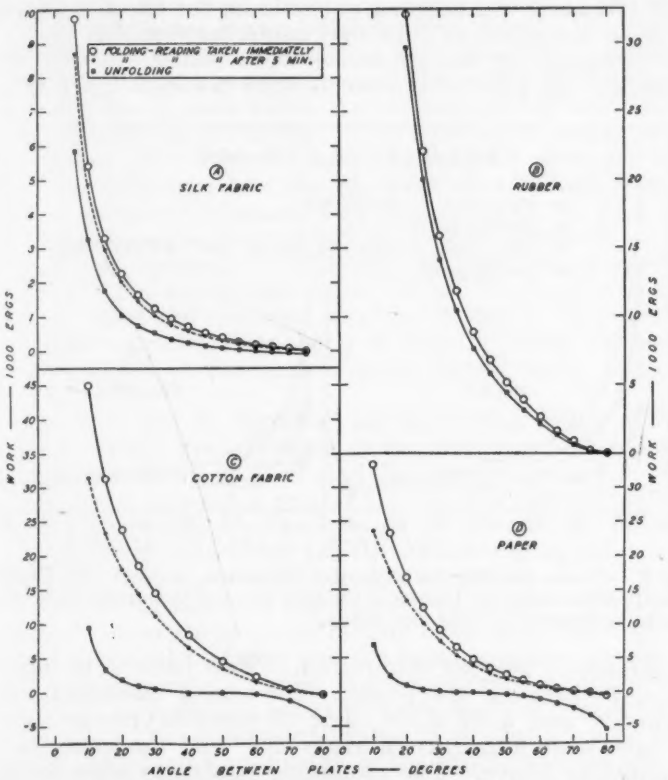


FIGURE 4.—*Typical curves for the folding and the unfolding of test specimens.*

testing. The curves in figures 3 and 4 were obtained by using a spiral spring, and those in figure 5 by using a cantilever spring. All tests were made on specimens in equilibrium with an atmosphere of 65 percent relative humidity at a temperature of 70° F.

In folding a specimen in the angle between the plates of the flexometer the spring deflection was determined when a given angle between the plates was approached from opposite directions; that is, when a specimen was folded to an angle of say 30° between the plates, the spring deflection was read as the angle was decreased to 30°. Immediately thereafter the angle was decreased 0.5° and the spring deflection was again read as the angle was increased to 30°. The

same procedure was followed at the other angles during folding. The data given in this paper for folding are based upon the first of these two readings. In unfolding the specimen a similar procedure was followed, namely, when the specimen was allowed to unfold to an angle of say 30° between the plates, the spring deflection was read as the angle was increased to 30°. Immediately thereafter the angle was increased 0.5° and the spring deflection was again read as the angle was decreased to 30°. The same procedure was followed at the other angles during unfolding. The data given in this paper for unfolding are based upon the last of these two readings. In other words, the data given in this paper are based upon the spring deflections obtained when the movable plate was rotated clockwise. This method of testing was adopted to eliminate the effect of friction.

To show the effect of time and angle between the plates on the torque developed by test specimens when folded, the following tests were made: Six pairs of specimens were cut from a silk fabric with

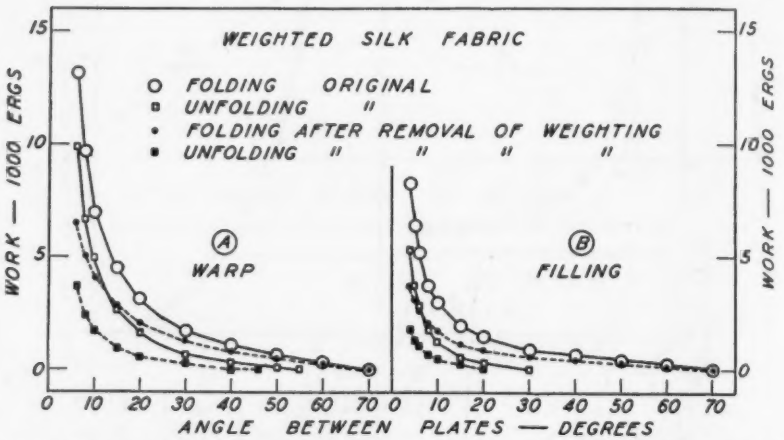


FIGURE 5.—*Curves showing the difference between a weighted silk fabric and the same silk from which the weighting has been removed chemically and the difference between the behavior of warp and filling.*

warp threads in lengthwise direction. Two pairs were folded to an angle of 7° between the plates. The spring deflection was noted immediately and after 5, 10, and 15 minutes, respectively. Two other pairs were folded to an angle of 9° and the spring deflections were noted as above. The remaining two pairs were folded to an angle of 11° and the spring deflections were again noted as above. The torques corresponding to these spring deflections were obtained from the calibration table. The results are shown graphically in figure 3. The torque is plotted as the ordinate. It is expressed in ergs per degree; that is, the work, in ergs, that would be done if the torque acted through one degree. The variation in duplicate determinations is shown by the solid and open circles.

The curves in figure 3 show how the torque decreases with time when a pair of specimens of a silk fabric are folded to given angles between the plates. The greatest decrease in the torque occurs during the first 5 minutes and at the smaller angle. Only a small additional decrease in torque would be expected after 15 minutes.

Similar measurements indicate that the decrease in torque is more pronounced for cotton fabric and paper, while no measurable decrease is observed for rubber. This is brought out in figure 4, where the work done on the test specimens in folding them to a given angle between the plates is plotted as ordinate and the angle as abscissa. The torque developed at any angle is equal therefore to the slope of the curve at that angle.

The curves *A*, figure 4, are for a silk fabric in which the warp threads were folded. A pair of specimens was folded to a given angle between the plates and the spring deflection was noted. The specimens were kept folded at this angle and the spring deflection was again noted at the end of 5 minutes. The angle between the plates was decreased 5° at a time and the spring deflections were noted as above. The results are shown by the curves through the circles and solid circles, respectively. The spring deflections were also obtained at the same angles during unfolding and the results are shown by the curve through the squares where the ordinate at any angle indicates the work recovered in unfolding. The decrease in spring deflection (torque) during the 5 minutes indicates that the specimen is being creased. The difference between the work done in folding and that recovered in unfolding expressed as a percentage of the work done in folding is related to the creaseability of the test specimen.

The curves, *B*, figure 4, are for folding and unfolding a specimen of sheet rubber. The spring deflections did not decrease by a measurable amount when the specimen was kept folded at each angle for 5 minutes. The curve for unfolding is slightly below the curve for folding, 92 percent of the work done in folding being recovered in unfolding.

The curves *C* and *D*, figure 4, are for cotton fabric and paper, respectively. They were obtained in the same manner as the curves for a silk fabric shown in 4, *A*, and for sheet rubber in 4, *B*. The spring deflections decrease a greater amount when specimens of these materials are kept folded at each angle for 5 minutes. The curves for unfolding are greatly below the curves for folding, indicating that these materials are more easily creased. Approximately 25 percent of the work done in folding is recovered in unfolding. The specimens unfold only to approximately 45° instead of to the initial angle of 80°. The crease in the cotton fabric and the paper specimens is not readily removed. To completely unfold these specimens to 80°, work must be done which is shown as negative work recovered in their curves for unfolding. The permanent crease and the amount of work necessary to unfold the specimens to the initial position are related to the creaseability of the specimens.

The curves *A*, *C*, and *D*, figure 4, show that the torque developed by the specimens of these materials when folded to a given angle between the plates decreases with the length of time the specimens are kept folded at that angle.

The curves in figure 5 show the difference between a weighted silk fabric and the same silk from which the weighting has been removed. The difference between the behavior of warp and filling is also shown. Specimens for test were taken from a tin-weighted silk, weighing 4.7 ounces per square yard and containing approximately 50 percent weighting material, and from the same fabric after the weighting materials had been removed chemically. The results for the warp

and filling are shown in *A* and *B*, respectively. The curve through the circles shows the amount of work in ergs done in folding a pair of specimens to various angles between the plates. The curve through the squares shows the amount of work recovered during unfolding. The dotted curves through the solid circles and squares are for the folding and unfolding of a pair of specimens taken from the same fabric after the weighting materials had been removed chemically.

IV. DISCUSSION

In order to assign numerical values to the flexural work, flexural resilience, and flexural hysteresis of different kinds of cloth or other materials to which the method is applicable, the dimensions of the test specimen and the minimum angle to which the specimen is folded between the plates of the flexometer must be specified. The dimensions specified, 4 inches long and 1¾ inches wide, were chosen simply because of their convenience. The angle to which the specimen is folded may not be chosen arbitrarily for it depends upon the thickness of the specimen. Thus a thick specimen cannot be folded in the flexometer to so acute an angle as a thin one and the angle which gives satisfactorily measurable results for a thick specimen may not be acute enough to give accurate results for a thin specimen.

In order to determine the angle to which a given specimen shall be folded, the assumption can be made that this angle is proportional to the thickness of the specimen. That this assumption is acceptable would be difficult to demonstrate for textile fabrics because of their complicated heterogeneous structure. However, it can be shown that the assumption is a good approximation for specimens of homogeneous isotropic material when the minimum angle between the plates is between 4° and 12°. For, if a thin specimen of homogenoeus isotropic material is bent in a principal plane by forces applied at the ends only, then the shape of the plane curve of the central line is an inflexional elastica, whereas if it is bent in a principal plane by couples applied at the ends only, then the plane curve of the central line is an arc of a circle.[11] Rigorous and approximate formulas for the inflexional elastica and for the circular arc are given below. For each case it is assumed that the results obtained are comparable when specimens of the same material but of different thicknesses are bent until the maximum tensile stresses are equal. The last assumption simply imposes the condition that the specimens of different thicknesses, h, are bent until the minimum radius of curvature, ρ_m, of the neutral surface [12] is equal to some constant, n, times the thickness h, or $\rho_m = nh$.

Let O in figure 6 be the center of the spindle, OM the movable plate, and OF the fixed plate. The angle between these two plates at any instant is denoted by β. Let $N\ P\ H^1\ P^1\ N^1$ be the central line of the specimen when it assumes the shape of the inflexional elastica, and let $N\ P\ H\ P^1\ N^1$ be the central line of the specimen when it assumes the shape of a circular arc. Let h be the thickness, $2\ P\ Q$, of the specimen, S_e the arc $P\ H^1\ P^1$ of the specimen for the inflexional elastica, and ρ_m the minimum radius of curvature. Let S_c be the arc $P\ H\ P^1$ of the specimen for the circular arc of radius r. Then it follows that

[11] The Mathematical Theory of Elasticity, by Love, 4th ed., pp. 399–404.

[12] By neutral surface of a bent specimen is meant that surface in which the elements suffer no deformation in the direction of length. For a homogeneous specimen it is midway between the two external surfaces.

$$r=\frac{L-l-\frac{h}{2}\tan\alpha}{\tan\alpha-\alpha}$$

$S_c=2\alpha r$ for the circular arc and

$$\rho_m=\frac{(L-l-\frac{h}{2}\tan\alpha)\cos\alpha}{2\sin{}^{\alpha}/_{2}\,[2E\text{ am }K-(1+\cos\alpha)\,K]}$$

$S_e=4\rho_m\ K\sin{}^{\alpha}/_{2}$ for the arc of the inflexional elastica where E and K denote the elliptic integrals of the second and first kind with

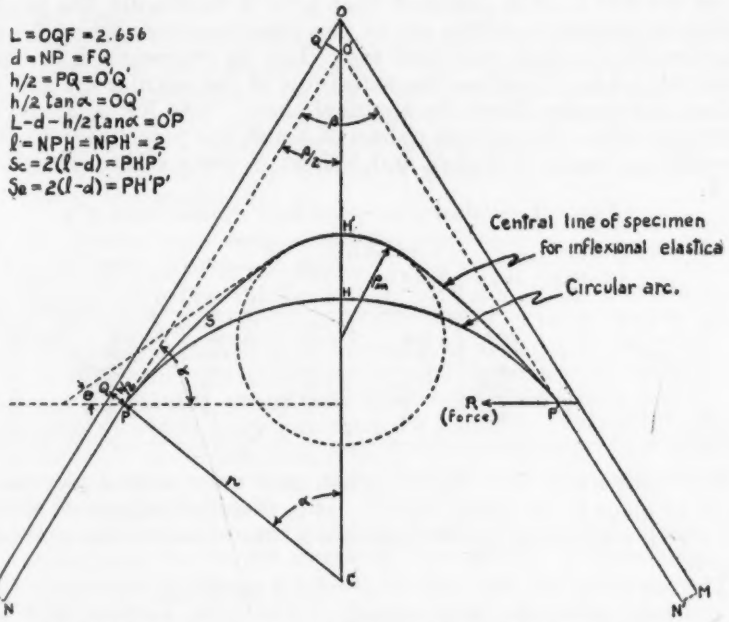


FIGURE 6.—*Schematic diagram of test specimen and intersecting plates.*

modulus k given by the equation $k=\sin{}^{\alpha}/_{2}$.[13] The symbols L and l are constants, L being one half the length of the movable plate, or 2.656 inches, and l one half the length of the specimen, or 2 inches. The angle α is the complement of ${}^{\beta}/_{2}$.

The formula $\rho=2\ h$ represents r within ± 6 percent for all values of β between 4° and 12° and the formula $S=6.2\ h$ represents S_e within ± 8 percent for all values of β between 4° and 20° provided $\beta=400\ h$. The formula $\rho=2\ h$ represents ρ_m within ± 6 percent for all values of β between 4° and 12° and $S=10\ h$ represents S_e within ± 6 percent for all values of β between 4° and 16° provided $\beta=460\ h$. The angle β, $2(90-\alpha)$, is measured in degrees, and the thickness h is measured in inches.

Similar approximate formulas may be obtained when ρ is taken equal to some other constant times h. The value 2 was chosen for

[13] See footnote 11, p. 654.

the constant n because for this value the magnitudes of the quantities measured for very thin specimens were such as to be easily measured and reproduced.

The results given above justify the assumption that the minimum angle between the plates should be proportional to the thickness of the specimen regardless of whether we assume the shape of the bent specimen to be circular or that of the inflexional elastica.

As previously mentioned, textile fabrics have a complicated heterogeneous structure. The arc of the bent specimen probably assumes a shape which lies somewhere between that of the inflexional elastica and the circle. Since $\rho=2\ h$ represents very closely the radius of the circular arc when $\beta=400\ h$ and represents very closely the minimum radius of curvature of the inflexional elastica when $\beta=460\ h$, it is assumed that $\rho=2\ h$ represents the minimum radius of curvature of the arc of the bent specimen when $\beta=430\ h$. The arc of the bent specimen may then be represented by the formula $S=8.6\ h$. To show the variations of the circular arc and of the inflexional elastica from the assumed shape, data for β, ρ, and S are given in table 1 for various values of h and the percentage variations of r and ρ_m from ρ, and of S_c and S_e from S, are given for these values of h.

TABLE 1.—*Values of β, ρ, and S for various values of h*

h	$\beta=430\ h$	$\rho=2\ h$	$S=8.6\ h$	$\frac{(r-\rho)100}{\rho}$	$\frac{(\rho_m-\rho)100}{\rho}$	$\frac{(S_c-S)100}{S}$	$\frac{(S_e-S)100}{S}$
Inch	°	*Inch*	*Inch*	*Percent*	*Percent*	*Percent*	*Percent*
0.0093	4	0.0186	0.08	4	−13	−26	3
.0186	8	.0372	.16	10	−8	−23	7
.0279	12	.0558	.24	17	−2	−20	10
.0372	16	.0744	.32	24	4	−18	14
.0465	20	.0930	.40	32	11	−15	19

The thickness [14] of a textile fabric may vary several percent from place to place in the same fabric. It is therefore suggested that it is not worth while to measure the angle β closer than to the nearest half degree.

The arc given by the formula $S=8.6\ h$ probably represents the arc of the bent specimen fairly closely. The area, volume, and weight of the arc of the bent specimen are therefore known with the same degree of approximation. The work done on the arc, S, of the bent specimen may thus be expressed in terms of unit width, unit cross section, unit arc, unit area, unit volume, or weight per unit area.

The following definitions based on the foregoing discussion may now be proposed for the standardization of numerical expression of three physical attributes of fabrics.

The flexural work of a fabric shall be the amount of work in ergs done in folding a specimen 4 inches long by 1¾ inches wide to an angle β, measured in degrees, which is determined by the thickness of the specimen, h, measured in inches, according to the equation $\beta=430\ h$.

The flexural resilience of a fabric shall be the amount of work recovered when the specimen which is folded as described above is allowed to unfold, expressed as a percentage of the work done in folding the specimen.

[14] Thickness shall be measured according to the standard method. See footnote 6, p. 648.

The flexural hysteresis of a fabric shall be the amount of work lost when the specimen is folded and allowed to unfold as described above, expressed as a percentage of the work done in folding the specimen.

It is evidently necessary in applying these definitions to specify the time consumed in folding and unfolding the specimen and the time it is allowed to remain folded. The previous history of the area included in the specimen is important. Imperfections of weave, creases, and other deformities may be expected to affect the result. A specimen taken from a small roll of cloth or from a folded area will not be representative of other portions that may have been kept flat. It is assumed that tests made with the flexometer will be carried out on specimens that are in equilibrium with an atmosphere of 65 percent relative humidity at a temperature of 70° F., the standard conditions for textile testing.

The flexometer should find use in the specification of the properties of fabrics required for given purposes. Mills which modify the flexural properties by sizing, weighting, and finishing operations may find in the flexometer a useful tool for the control of processes and standardization of products. The flexometer should make possible quantitative studies of effect of variations in processes upon the flexural properties of the products.

V. SUMMARY

An instrument called the flexometer with which the flexural work, flexural resilience, and flexural hysteresis of fabrics, paper, sheet rubber, and similar materials can be evaluated is described. Typical results in the form of curves showing the flexural characteristics of cotton and silk fabrics, paper, and sheet rubber are given.

The angle to which specimens must be folded to obtain comparable results depends upon the thickness of the specimens. An equation for determining the minimum angle for any given thickness of specimen has been developed.

Drawings of the flexometer showing the details of construction may be obtained from the textile section of the Bureau of Standards.

WASHINGTON, March 13, 1933.

A METHOD OF EXCITING RESONANT VIBRATIONS IN MECHANICAL SYSTEMS

By L. B. Tuckerman, H. L. Dryden, and H. B. Brooks

ABSTRACT

This brief note describes the essential features of a method of exciting resonant vibrations in mechanical systems, developed for the study of the vibrations of aircraft propellers.

In the study of the vibrations of aircraft propellers, a method of exciting resonant vibrations has been devised which may find application to other mechanical systems. We are therefore publishing this brief description.

It was desired to study the vibrations which might be caused by the periodic variations in torque of an aircraft engine due to the explosions in the individual cylinders, or by the passage of the blades past struts or other asymmetric parts of the airplane structure. Because of the inertial and aerodynamic coupling between the rotational motion of the shaft and the flexural motion of the propeller blade, strong vibrations of the propeller blade may be set up if the period of the torque impulses coincides with a natural frequency of vibration of the blade. The stresses set up by such resonant vibrations may be sufficient to cause failure of the propeller.

As the first stage in the study of these vibrations, attention has been confined to nonrotating propellers. It is of course possible to apply periodic inpulses by means of a mechanically driven system employing either a group of rotating unbalanced weights or a direct drive from a crank and connecting rod. We were, however, early attracted to an electromagnetic drive because of the ease with which the frequency and magnitude of the variation of torque could be independently controlled. The primary electrical equipment required is an alternator driven by a variable speed d.c. motor, the frequency being adjusted by adjusting the speed of the driving motor and the magnitude of the impulses being regulated by the excitation of the field of the alternator.

When the design of the electromagnetic drive was under consideration, it occurred to one of us that there was already existent an efficient device for the utilization of electric current to produce mechanical torque, namely, an ordinary direct-current motor. To produce alternating torque instead of a steady torque it is only necessary to supply alternating current to the armature instead of direct current, the field being supplied with direct current in the usual manner. Unless large angular motions are to be utilized (possible only at very low frequencies because of the inertia of the armature), no modification

in the direct-current motor is required. If large motions are to be permitted, flexible leads or slip rings may be attached to two bars of the commutator at a spacing equal to the spacing of the field poles.

We have set up such a system, using a 7½ horsepower d.c. motor. With this comparatively small motor and an alternator and driving motor which were available we have been able to produce resonant vibrations of sufficient intensity to break ordinary propeller blades in from 5 to 10 hours. The breaks were typical fatigue breaks.

At present the equipment is being used to study the stress distribution in the vibrating propellers. Tuckerman optical strain gages are mounted on the blade, and the relations between the strain amplitude and tip amplitude of the vibration are determined for different amplitudes and frequencies and different positions along the blades.

It is found that for any given position and frequency the strain amplitude is proportional to the tip amplitude. With frequencies varied from 20 percent below up to 10 percent above the lowest resonant frequency, the strain distribution along the blade for a given tip amplitude is not greatly changed.

The apparatus is now being modified to study the strain distribution at higher resonant frequencies.

With this equipment it is also possible to determine the tip amplitude of vibrations produced by a known variation of torque and hence the stress distribution throughout the blade for a known torque variation. The stresses due to vibration may be combined with the direct bending and centrifugal stresses computed in the usual manner and if the strength of the material under combined alternating and direct stress is known, the factor of safety of the design may be determined.

It is quite possible to extend the system to rotating propellers, using, of course, a much larger d.c. motor supplied with d.c. current to rotate the propeller at its rated speed, the alternating current being introduced through a transformer. The measurement of strain distribution in rotating propellers is, however, still an unsolved problem.

WASHINGTON, March 13, 1933.

RP557

CONDITIONS AFFECTING THE FREEZING TEMPERATURE OF SILVER

By Wm. F. Roeser and A. I. Dahl

ABSTRACT

A study was made of the precautions which should be observed in using the freezing point of silver as a thermometric fixed point. Observations were made on three samples of silver containing various amounts of impurities. The depression of the freezing point due to absorption of oxygen was measured under a number of conditions. It was found that graphite crucibles and covers were as effective in protecting silver from oxygen as a vacuum 0.005 to 0.03 mm of Hg.

CONTENTS

	Page
I. Introduction	661
II. Methods	662
III. Results	665
IV. Discussion of results	667
V. Summary	668

I. INTRODUCTION

The International Temperature Scale [1] is defined in the range 660° to 1,063° C. in terms of the indications of a platinum to platinum-10 percent rhodium thermocouple calibrated at three thermometric points—the freezing points of gold, silver, and antimony. In order that the scale so defined may be definite and reproducible, it is necessary not only that the metals used be of high purity so that variations due to differences in the metals themselves be eliminated as far as possible but also that the conditions under which the metals are frozen be sufficiently definite to eliminate significant differences from this cause.

Comparisons [2] of the International Temperature Scale as realized at the Bureau of Standards in this country, at the National Physical Laboratory in England, and at the Physikalisch-Technische Reichsanstalt in Germany have indicated that both of these requirements have been met in the case of the gold and antimony points. It was found, however, that the same thermocouple, when immersed successively in the crucibles of freezing silver employed as the temperature standards by the three national laboratories, yielded emfs differing by more than the amount which could be ascribed to accidental errors. The emf differences were equivalent to approximately 0.5° C. It was thought that these discrepancies were due in part to differences in experimental procedure. At the Bureau of Standards and the

[1] Proc. Seventh General Conference of Weights and Measures, 1927, p. 56. Text in annex IV, p. 94.
G. K. Burgess, B. S. Jour. Research, vol. 1, p. 635, October 1928.
[2] B.S.Jour. Research (subsequent publication).

Physikalisch-Technische Reichsanstalt the freezing silver is contained in a covered graphite crucible. The atmosphere is presumed to be principally nitrogen, carbon monoxide, and carbon dioxide. At the National Physical Laboratory the silver is frozen in vacuo.

All the work available in the literature indicates that the three gases—nitrogen, carbon monoxide and carbon dioxide—are not appreciably soluble in this metal. However, it is well known that molten silver, exposed to an atmosphere containing oxygen, will absorb oxygen and that the freezing point of the metal will thereby be changed by an amount depending upon the quantity absorbed. Calculation by van't Hoff's equation shows that it requires but 0.007 percent of dissolved oxygen by weight to lower the freezing point of silver 0.5° C. which was the magnitude of the discrepancies among the various laboratories. The work of Sieverts and Hagenacker[3] indicates that this amount of oxygen would be absorbed by molten silver in equilibrium with oxygen at a pressure of 0.4 mm of Hg. There have been no observations reported on the freezing point of silver in vacuo at pressures of 0.4 mm of Hg or less.

The present investigation was originally undertaken to determine the source of the discrepancies among the results obtained by the various laboratories at the freezing point of silver. Although early in the investigation it was found that the above-mentioned discrepancies were due primarily, if not wholly, to metallic impurities, the investigation was completed as planned in order to show (1) the difference in the freezing points of various lots of silver, including that used by Day and Sosman in the determination with the gas thermometer which led to the adoption of 960.5° C. for this point; (2) the effectiveness of graphite in protecting silver from oxygen and the effect of the other gases present when the metal is melted in graphite crucibles; (3) the amount of the depression of the freezing point when no precautions are taken to eliminate oxygen; (4) the amount of the depression when the silver is saturated with oxygen at the pressure prevailing in the atmosphere; and (5) the amount of the depression when the silver is saturated with oxygen at the pressure of 1 atmosphere.

It is recognized that the freezing point of any substance depends upon the pressure, but a calculation using Clapeyron's equation reveals that the freezing point of silver is only 0.005° C. lower in vacuo than at a pressure of 1 atmosphere. Since the instruments used in this investigation are not accurate to better than 0.02° C., differences in the freezing point due to changes in the pressure, may be neglected.

II. METHODS

Three samples of silver were available for the investigation: (1) The silver which had been in use at the Bureau of Standards for five years and which is designated "old silver"; (2) a new lot of greater purity than the above, obtained from the United States Bureau of the Mint, and known as "inquartation silver"; and (3) the sample used by Day and Sosman[4] in their work with the nitrogen gas thermometer. The cooperation extended by Dr. A. L. Day, of the Geophysical Laboratory, in lending us this sample of silver is gratefully acknowledged.

The analyses of the various samples of silver are given in table 1.

[3] Sieverts and Hagenacker, Zeits. fur Phys. Chem., vol. 68, p. 115, 1910.
[4] Day and Sosman, Car. Inst. of Wash., Pub. No. 157, 1911; Am.J.Sci., vol. 33, p. 517, 1912.

TABLE 1.—*Analyses of silver samples*

Element sought	Percent of impurities		
	Old silver [1]	Inquartation silver [1]	Day and Sosman silver [2]
Cu	0.0680	0.0020	Mere trace
Pb	.0005	.0050	0.0008
Fe	.0003	.0010	.0011
Au	Not detected	Not detected	.0005
Pt	Not detected	Not detected	.0001
Ni	Not detected	Not detected	Not detected
Zn	Not detected	Not detected	Not detected
S			.0004
C			.0003
As			Not detected
Sb			Not detected
Sn			Not detected
Bi			Not detected
Hg			Not detected
Cd			Not detected
Co			Not detected
Total	.0688	.0080	.0032
Silver by difference	99.931	99.992	99.997

[1] By J. A. Scherrer, Chemistry Division, Bureau of Standards.
[2] From An Investigation of the Metals, by E. T. Allen, in High Temperature Gas Thermometry, The Carnegie Institution of Washington, Publication No. 157.

The four platinum to platinum-10 percent rhodium thermocouples used in this investigation were taken from the same lots of wire, and consequently had practically identical characteristics. The thermoelectric power (microvolts per ° C.) for thermocouple G_2 ($dE/dt = 8.298 + 0.003235\ t$) obtained from calibration in accordance with the specifications of the International Temperature Scale, may be used for the other couples without introducing errors greater than 0.2 percent. This is sufficiently accurate, since the other couples were only used for measuring temperature differences of the order of 0.5° C.

The measurements may be divided into six groups. In the first series of measurements the difference between the freezing points of the "old silver" and the "inquartation silver" in graphite crucibles was measured, using the same equipment and following the same procedure as described in a previous publication.[5]

In the second series of measurements the differences between the freezing points of the "old silver", the "inquartation silver", and the Day and Sosman silver in graphite crucibles were measured, using an electric furnace 3.8 cm in diameter and 25 cm long. Smaller samples were used in this case, crucibles 2.2 cm inside diameter and 10 cm deep, since the mass of the sample of silver obtained from Dr. Day was only about 200 g, and in order to obtain the highest accuracy in the measurement of temperatures with thermocouples, it is necessary to use the couples at the same depth of immersion during any series of measurements.

In the third series of measurements samples of the "old silver" and "inquartation silver" in graphite crucibles 3 cm inside diameter and 15 cm deep were placed successively in a silica tube, as shown in figure 1. For obtaining observations at the freezing points in vacuo,

[5] Wm. F. Roeser, B.S.Jour. Research, vol. 3, p. 343, 1929.

the silica tube was closed at the top by a pyrex glass cap. The silver was melted and the thermocouple protection tube then lowered into the silver to a depth of 10 cm. The cap was sealed to the silica tube and the protection tube by means of De Khotinsky cement. The silica tube was then evacuated by means of a 2-stage mercury diffusion

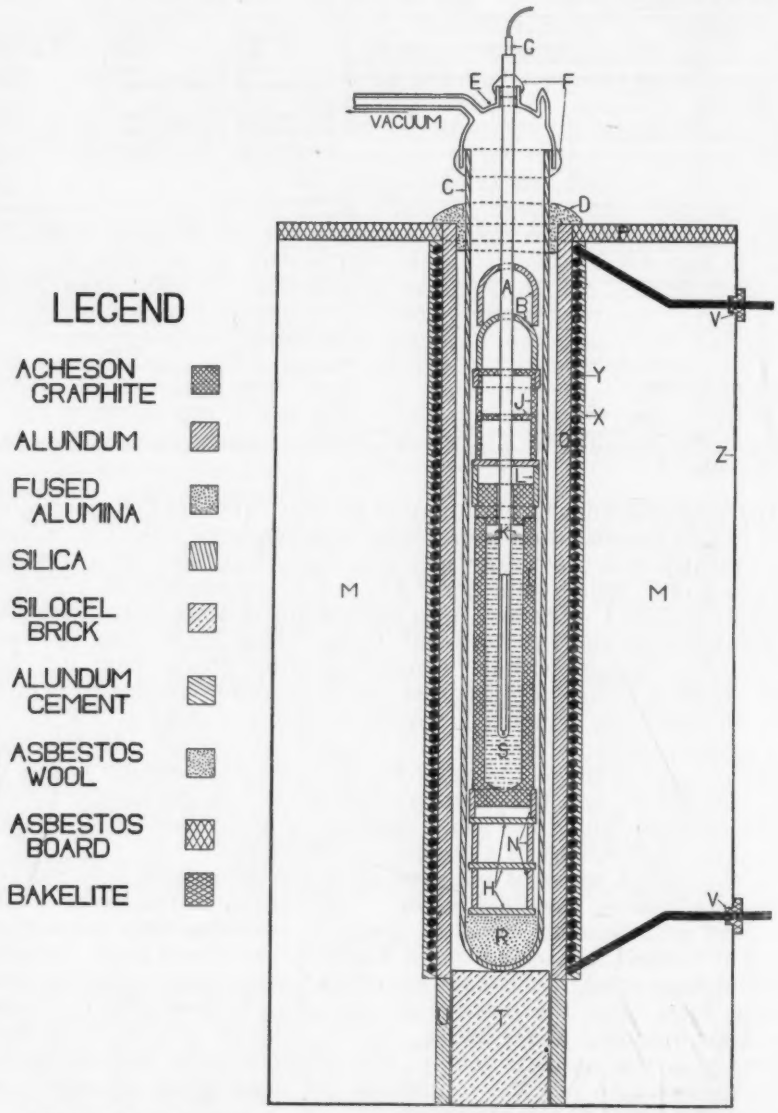


FIGURE 1.—*Arrangement for obtaining freezing point of silver in vacuo.*

pump backed by a Cenco Hyvac pump. A liquid air trap was placed between the pump and the silica tube. After completing the observations on a sample in vacuo, the cap was removed and similar measurements made with the tube open to the atmosphere. These measurements on the two samples of silver duplicated the first series

of measurements in addition to yielding the difference between the freezing point of each sample in vacuo and in a graphite crucible exposed to the atmosphere. The samples of silver used in these measurements were from the same lots of silver, though not the identical samples used in the first series.

In the fourth series of measurements the sample of "old silver" used in the third series was placed in a porcelain crucible at the same location in the furnace as before. Observations were taken at the freezing point with no provision for preventing access of oxygen, the silica tube being open to the atmosphere.

The fifth series of measurements was very similar to the fourth, with the exception that air was bubbled through the molten silver for various intervals of time preceding the freeze. The air was carried to the bottom of the silver by means of a porcelain tube which was removed a few seconds before freezing began.

The sixth series of measurements was the same as the fifth, with the exception that pure oxygen was bubbled through the molten silver. Since the pressure of the oxygen was slightly greater than that of the atmosphere and since the opening to the atmosphere was restricted by the diaphragms, the gas above the silver was practically all oxygen at a pressure of about 1 atmosphere.

In any series of measurements the thermocouples were immersed in the silver and in the furnace to the same depth. The cold junctions were maintained at 0° C. and the electromotive forces of the couples were read to 0.1 μv (approximately 0.01° C.).

III. RESULTS

The observed differences between the freezing points of the "old silver" and the "inquartation silver" are given in table 2.

TABLE 2.—*Differences in freezing points of "old silver" and "inquartation silver" in graphite crucibles*

Experiment No.	Air pressure above crucible	Freezing point "inquartation silver" minus freezing point "old silver"				
		Thermocouple				Mean
		G_1	G_2	G_{11}	G_{12}	
		°C.	°C.	°C.	°C.	°C.
1	Atmospheric	0.40	0.39	0.40	0.40	0.40
2	do		.65			.65
3	do	.53	.54	.49	.40	.49
3	0.03 to 0.005 mm of Hg	.56	.53	.51	.47	.52
Average difference.		0.5° C.				

Since different samples were used in each experiment, part of the differences in the values obtained in the various experiments are probably due to variations in the samples. The average value of 0.5° C. is probably good to ±0.1° C.

The freezing point of the Day and Sosman silver under identical conditions was found to be 0.01° C. higher than that of the "inquartation silver." Only one thermocouple, G_2, was used in these measure-

ments but this couple was the most homogeneous of the lot and therefore best adapted to the measurement of such small differences.

The observed differences between the freezing points of silver in vacuo and in graphite crucibles exposed to the atmosphere are given in table 3.

TABLE 3.—*Difference between freezing points of silver in vacuo (0.03 to 0.005 mm of Hg) and in air with graphite protection*

Silver	Freezing point in graphite crucibles minus freezing point in vacuo				
	Thermocouple				Mean
	G_1	G_2	G_{11}	G_{12}	
	°C.	°C.	°C.	°C.	°C.
"Inquartation"	0.06	0.02	0.04	0.04	0.04
"Old"	.11	.01	.05	.10	.07
Average difference	0.05° C.				

The effect of pressure alone would account for only one-tenth of this difference. Since the temperature gradients in both the furnace and the thermocouple wires in the determination at low pressure were appreciably different from those prevailing in the measurements at atmospheric pressure, the measurements are not believed to be accurate to better than 0.05° C. However, the observations with thermocouple G_2 lead us to believe that the freezing point of silver in vacuo does not differ significantly from that in graphite crucibles.

The observed depressions of the freezing point of silver, in a porcelain crucible, when merely exposed to air and when air or oxygen is bubbled through the molten metal previous to freezing are summarized in table 4. Only the "old silver" and thermocouple G_2 were used in these measurements.

TABLE 4.—*Depression of the freezing point of silver by absorbed oxygen*

	Depression ° C.
Silver in porcelain crucible, surface exposed to air	1.5
Air bubbled through silver for 25 minutes	7.2
Air bubbled through silver for 30 minutes	8.0
Air bubbled through silver for 40 minutes	6.7
Air bubbled through silver for 70 minutes	11.2
Air bubbled through silver for 120 minutes	11.3
Oxygen bubbled through silver for 1 minute	5.4
Oxygen bubbled through silver for 50 minutes	22.6

No difficulty was encountered in reproducing the depressions of 11.2° and 22.6°, which leads to the conclusion that the silver was saturated with oxygen at the prevailing pressures (approximately 140 and 760 mm of Hg, respectively).

The freezing curves obtained under some of these various conditions are shown in figure 2. The freezing point was taken as the temperature corresponding to the initial freezing in each case.

IV. DISCUSSION OF RESULTS

As pointed out earlier, this investigation was undertaken to determine the differences in the freezing point of silver under different experimental conditions. Such questions can be settled only by experiments. Values for some of the differences measured may be computed from the chemical analyses of the silver samples, the

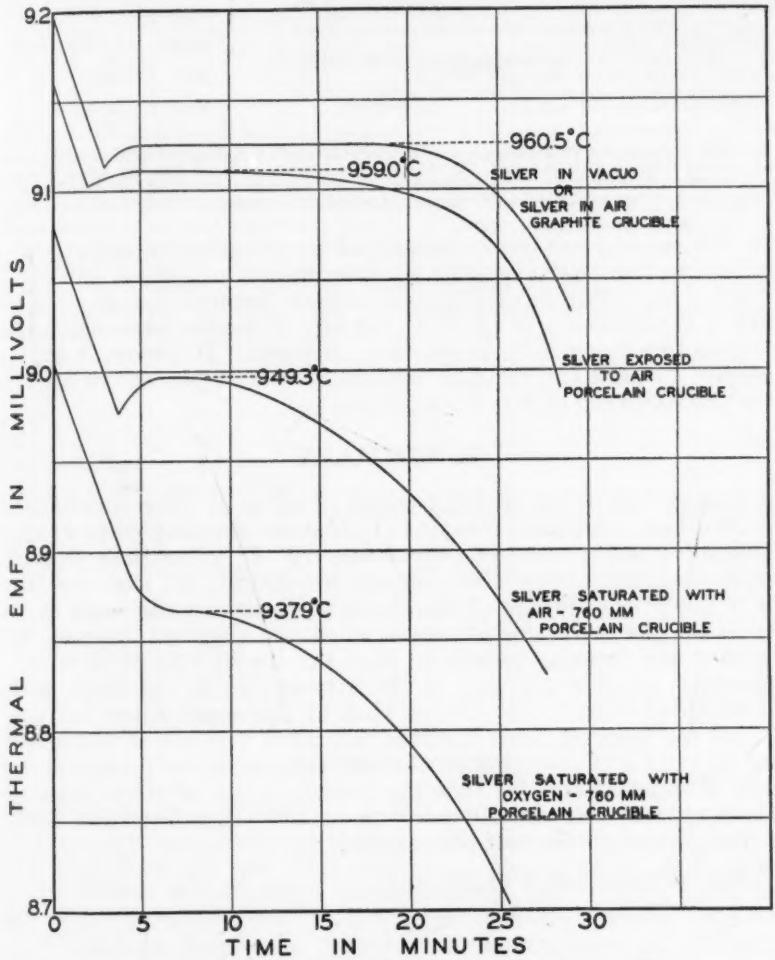


FIGURE 2.—*Freezing curves of silver under various conditions.*

absorption of oxygen by silver, other data available in the literature, and certain assumptions regarding the solution of impurities. The test of the applicability of such calculations is their agreement with experiments.

The computed and observed values are given in table 5, together with the estimated accuracy of the observed values. In the computations the latent heat of fusion of silver was taken to be 2,790 calories per gram-atom.

TABLE 5.—*Comparison of computed and observed values*

	Computed	Observed	Estimated accuracy of determination
	°C.	°C.	°C.
Freezing point of Day and Sosman minus freezing point of "inquartation silver"	0.01 or 0.05	0.01	0.05
Freezing point of "inquartation silver minus freezing point of old silver"	[1] 1.18	.5	.1
Freezing point of silver in graphite (atmospheric pressure) minus freezing point in vacuo	.005	.05	.05
Freezing point of silver in graphite minus freezing point of silver saturated with air (760 mm Hg)	10.2	11.2	.5
Freezing point of silver in graphite minus freezing point of silver saturated with oxygen (760 mm Hg)	22.3	22.6	.5

[1] This value is based upon the hypotheses that the dissolved copper is monatomic and that mixed crystals are not formed to an appreciable extent. If either of these hypotheses is not true, the actual depression will be less than that calculated. The equilibrium diagram for copper and silver indicates that mixed crystals are formed and that the initial freezing point of silver is lowered 0.5° C. by 0.068 percent of copper.

In the methods generally employed in obtaining observations at the freezing point of silver, the silver is molten for only a short time, and since the diffusion of absorbed oxygen through the silver is evidently a slow process, it appears that any of the methods now in use for protecting silver from oxygen are adequate. However, it appears necessary to limit the metallic impurities to 0.01 percent in order to obtain an accuracy of 0.1° C.

V. SUMMARY

A comparison of the freezing points of silver of three lots of silver under various conditions revealed (1) that the freezing point of silver containing 0.068 percent of copper was 0.5° C. lower than that of a sample containing only 0.008 percent impurities; (2) that the silver now in use at the Bureau of Standards is essentially the same as that used in the gas thermometer measurements of Day and Sosman, both in purity and freezing point; (3) that the freezing point of silver in a graphite crucible exposed to the atmosphere is the same within experimental error (0.05° C.) as that of the same silver in vacuo; (4) that the freezing point of silver saturated with air at 760 mm Hg pressure is 11.2° C. lower than that of the same silver protected from access of oxygen; and (5) that the freezing point of silver saturated with oxygen at 760 mm Hg pressure is 22.6° C. lower than that of the same silver protected from oxygen.

WASHINGTON, March 13, 1933.

RP558

LONG-WAVE ARC SPECTRA OF ALKALIS AND ALKALINE EARTHS

By William F. Meggers

ABSTRACT

New types of photographic plates sensitive to red and infrared radiation are employed to record the emission spectra of electric arcs containing alkalis or alkaline earths. Several lines characteristic of sodium, potassium, rubidium, and cesium are observed in the interval 8,500 to 11,800 A. A larger number of lines are measured in calcium, strontium, and barium spectra between the limits 6,500 and 11,300 A. Practically all of the observed lines are accounted for as combinations of identified spectral terms. A new system of band heads, presumably due to CaO, was found in the infrared.

CONTENTS

	Page
I. Introduction	669
II. Wave-length measurements	671
III. Results	672
1. Alkalis	672
(*a*) Lithium	673
(*b*) Sodium	673
(*c*) Potassium	673
(*d*) Rubidium	674
(*e*) Cesium	674
2. Alkaline earths	675
(*a*) Calcium	676
(*b*) Strontium	679
(*c*) Barium	680

I. INTRODUCTION

Seventeen years ago I had the good fortune to be among the first to photograph infrared emission spectra with the aid of dicyanin which was at that time the best photosensitizing dye for the longer waves. The arc spectra of the alkalis, alkaline earths, and various other elements were photographed with a large concave grating, and the stronger infrared lines were recorded[1] to about 9,600 A. Now an opportunity to improve and extend these results has been created by the discovery, in the research laboratory of the Eastman Kodak Co., of vastly superior photosensitizing dyes.

Two new dyes are especially important; they have been named mesocyanine and xenocyanine. The former imparts a maximum sensitizing action at wave length 8,600 A, while the latter exhibits a very broad sensitizing band with a maximum at 9,700 A, and still appreciable beyond 12,000 A. With these materials a considerable range

[1] W. F. Meggers, B.S.Sci. Papers, vol. 14 (no. 312), p. 371, 1918.

of infrared spectra either unknown or explored heretofore only with radiometric devices become accessible to spectrography with all the advantages of high resolution and precision accompanying the photographic method. As an example of the application of improved photographic plates, new data on the red and infrared arc spectra of the alkalis and of the alkaline earths are reported in this paper.

The spectra of these elements have played an important part in the development of a theoretical interpretation of atomic spectra. Since alkali atoms possess a single valence electron and the alkaline earths only two, their spectra are of relatively simple types. Indeed, this is the reason that law and order was found in them nearly half a century ago, or shortly after the first significant connection between spectral lines was discovered for the visible lines of atomic hydrogen.

Analysis of the alkali spectra first suggested the general law that any spectral lines can be represented as the difference of two terms, any term being expressed in the form $T=R/(m+\mu)^2$, in which R has since been called the Rydberg constant, m is an integer subsequently recognized as the total-quantum number, and μ is a correction factor.

Furthermore, the discovery of series in the alkali spectra first disclosed the fact that several different types of series were present. Certain properties of these different types suggested their names ("principal", "sharp", "diffuse", "fundamental"), and the initial letters of these names have been retained in the modern notation for spectral terms. According to modern theory such series types are distinguished by the quantum number l, which in the planetary model of an atom represents the moment of momentum (in units of $h/2\pi$) of the valence electron coursing in its orbit; the l values are 0, 1, 2, 3, for S, P, D, F terms, respectively.

The pioneer studies of series in these spectra also brought out the fact that most spectral terms are complex or multiple. Spectral terms characteristic of alkalis are double, whereas those of the alkaline earths are either single or triple, but ionized atoms of the alkaline earths are again represented by doublets like the alkalis. Extension of these term multiplicities to other spectra later suggested the alternation and displacement laws of spectroscopy which now appear to be generally valid. In order to distinguish the various sublevels of a multiple term the so-called inner-quantum number "j" was empirically introduced almost 10 years ago, but it was several years later that its interpretation as the vector sum J of electron orbital momentum l and electron spin momentum s was first suggested by the doublet character of alkali spectra. Every electron is assumed to possess the same spin, which gives it an angular momentum of $sh/2\pi$ and since s always has a value of one half it follows that J values of spectral levels are always integers for odd multiplicities and half integers for even multiplicities.

Finally, analysis of the alkaline earth spectra, in the production of which two valence electrons are involved, indicated that when two (or more) electrons simultaneously play a part in radiation the quantum numbers L associated with various types of terms are to be considered as the vector sum of the l's of the individual electrons. This important discovery was the key to a complete theory of spectral terms correlated with electron configurations, now a guiding principle in the structural analysis of any atomic spectrum.

The alkali and alkaline earth spectra also have played a prominent role in the development of the theory of spectral line intensities and of

Zeeman effects, but it is unnecessary to cite any further examples to demonstrate the importance of complete and accurate descriptions of their spectra. However, despite numerous investigations during 70 years or more, it must be admitted today that improvement in the spectral data for all of these elements in still desirable. It can safely be said that scarcely any of the wave lengths are known to the third decimal in angstrom units, many of them are uncertain in the first decimal place and some are surely in error by one or more units. The results reported below represent preliminary observations of lines which either have not been recorded photographically heretofore or only with much smaller intensity and dispersion. The accuracy of the wave-length measurements may be increased only by employing sources giving sharper lines, and the estimated relative intensities should eventually be replaced by quantitative measurements.

II. WAVE-LENGTH MEASUREMENTS

The spectra here dealt with were derived from electric arcs at atmospheric pressure, the light being dispersed by large concave diffraction gratings and photographed with special types of sensitized emulsions. Chloride salts of the elements were used on graphite or on copper electrodes with an applied potential of 220 volts and direct current of 8 to 10 amperes in the arc. Bands due to carbon or its compounds which are very prominent and troublesome when graphite electrodes are used, are almost completely suppressed when an abundance of salt is present, but the difficulty with such bands was entirely eliminated by making duplicate exposures with copper electrodes. In the latter case the bands which appear are most likely due to oxides of the elements inserted in the arc.

Two concave diffraction gratings of 21.7 feet radius of curvature were employed as stigmatic spectrographs, the slit being at the principal focus of a stainless-steel mirror which then illuminates the grating with parallel light. One grating has 20,000 lines per inch and gives a scale of 3.5 A/mm, while the other has 7,500 per inch and a scale of 10.2 A/mm. The former was used in the interval 6,500 to 9,000 A, and the latter in the longer wave region from 8,500 to 12,000 A. The second is the identical grating and type of mounting employed in our earlier campaign on infrared spectra and has been described in detail elsewhere.[2]

Exposures of 30 to 60 minutes were made in the first-order spectra; the longer time designed to record faint or farther infrared lines always resulted in tremendous over-exposure of the spectrograms in the region of their maximum sensitiveness.

Eastman plates for spectroscopy have been described by C. E. K. Mees.[3] The N, P, and Q types of sensitizing were chosen for the exploration of alkaline earth spectra, but only Q plates were used on the alkalis. In other words, the arc spectra of Ca, Sr, and Ba have been photographed from the red at 6,500 A to the infrared beyond 11,000 A, but the alkali spectra were examined only in the region beyond 8,500 A. Each plate was hypersensitized in a dilute ammonia bath before use and developed in Eastman's X-ray developer after exposure. The red and infrared radiation was always recorded in

[1] W. F. Meggers and Keivin Burns, B.S. Sci. Papers, vol. 18 (no. 441), p. 191, 1922.
[2] C. E. K. Mees, J. Opt. Soc. Am., vol. 21, p. 753; 1931; vol. 22, p. 204; 1932. Addendum dated February 1932.

the first-order spectrum of the grating, the overlapping higher orders being removed by a deep-red glass filter. Adjacent to the first-order spectra on each spectrogram the arc spectrum of iron was recorded to supply standards for wave-length measurements. For the red to 8,000 A first-order comparison spectra were used, but the longer waves were measured against second- or third-order iron lines, the wave lengths being doubled or trebled to serve as first-order standards in accordance with the fundamental law of diffraction gratings. Most of the lines reported here were recorded on two or more spectrograms, and each spectrogram was measured in both directions, so that the wave length values for sharp lines in the range of larger dispersion (6,500 to 9,000 A) are expected to be correct within ± 0.01 A, while the probable errors of the remainder are several times larger on the average. Many of the lines are hazy, wide, and shaded either to longer or shorter waves; these characteristics are indicated in the tables by the letters *h*, *w*, *l*, and *v*, respectively.

III. RESULTS

1. ALKALIS

It is well known that the arc spectra of the alkali metals consist of doublets, in which the separations become larger with increasing atomic number. In general, also, the corresponding spectral series in the different elements are displaced toward longer waves as the atomic number increases. In each case the various series begin with their most intense lines in the red and infrared (detected by means of bolometers or thermopiles) and converge to limits in the ultraviolet or visible regions.[4] The first members of the principal, sharp, and diffuse series for each of the alkalis had already been recorded photographically with the following exceptions: sharp series of Na, K, Rb, Cs, and diffuse series of K, Rb, and Cs. Now with xenocyanine plates it has become possible to complete the photographic record for the sharp series of Na and for the diffuse series of K. The first members of the fundamental series still remain beyond photographic reach except for Cs, which is now easily recorded, while only the first lines are out of range for Rb and K, and all but the first two in Li and Na are now accessible to photography.

It seemed at first that observations of the fundamental series in alkali spectra might constitute the major portion of this contribution to infrared spectroscopy, but the expectations have been curtailed by the nature of the spectral lines. Fundamental series lines in general have a tendency toward excessive and unsymmetrical diffuseness, and this is especially true in alkali spectra when the source is an electric arc at atmospheric pressure. Diffuseness of the fundamental series lines is most marked in the lighter elements; the lines gradually become sharper with increasing atomic number, until in Cs they do not differ much in appearance from the so-called "diffuse-series" lines. This increasing homogeneity is no doubt due in part to the reduced Döppler-Fizeau width, but perhaps more to a smaller Stark effect as the limit

[4] Summaries of the spectral series for alkali metals were published by Paschen and Götze and by Fowler in 1922, several years before the quantum theory and the notation for spectral structures had been developed. The same data with revised notation are contained in handbooks by Grotrian and by Bacher and Goudsmit:
F. Paschen and R. Götze, Seriengesetze der Linienspektren, Julius Springer, Berlin, 1922.
A. Fowler, Report on Series in Line Spectra, Fleetway Press, London, 1922.
W. Grotrian, Handbuch der Astrophysik, III, pp. 475–602, Julius Springer, Berlin, 1930.
R. F. Bacher and S. Goudsmit, Atomic Energy States, McGraw-Hill Co., New York, 1933.

of the fundamental series sinks in the energy diagram and approaches that of the diffuse series.

(a) LITHIUM (Li, Z=3)

Only two lines of the fundamental series of Li have been detected radiometrically in the infrared; their approximate wave lengths are 18,697 and 12,782 A. The next succeeding lines are expected to have wave lengths of about 10,906, 10,017, 9,513 A, etc., all within the range of a xenocyanine plate. My Li spectrogram shows hazy patches at about these positions, but the lines are too diffuse to measure. In order to obtain useful wave lengths it will be necessary to use a vacuum arc or other source in which the fundamental series lines are more homogeneous.

(b) SODIUM (Na, Z=11)

As for Li, only two lines of the fundamental series of Na are known; their wave lengths are 18,460, 12,678 A. The succeeding lines are expected near 10,830, 9,894, 9,455 A, etc.; indications of them appear on my spectrograms, but they are too diffuse to permit of accurate measurement. The first member of the sharp series occurs near 11,400 A and is easily photographed, while a new combination is found near 10,746 A. The measured wave lengths' estimated intensities, vacuum wave numbers, and term combinations of these lines are presented in table 1.

TABLE 1.—*Arc spectrum of sodium*

Intensity	λ_{air} I.A.	ν_{vac} cm^{-1}	Term combination
10	11, 403. 96	8, 766. 49	$3^2P^\circ_{1/2}$–$4^2S_{1/2}$
6	11, 381. 62	8, 783. 69	$3^2P^\circ_{3/2}$–$4^2S_{1/2}$
2	10, 748. 7	9, 300. 9	$4^2S_{1/2}$–$5^2P^\circ_{3/2}$
4	10, 745. 9	9, 303. 3	$4^2S_{1/2}$–$5^2P^\circ_{1/2}$

(c) POTASSIUM (K, Z=19)

With xenocyanine plates no difficulty was experienced in recording in full detail the first lines of the diffuse series of K with wave lengths approaching 1.2 μ. This is an excellent example of two doublet terms combining to produce a multiplet of three lines, the levels of the ^2P term being separated 57.6 cm^{-1}, while an interval of 2.6 cm^{-1} occurs between the ^2D levels. These lines are reasonably sharp in the ordinary arc, because they involve relatively low energy states, but the remaining lines observed in the K arc involve higher levels and are consequently too diffuse and wide to permit definitive wave-length determinations. New data acquired with xenocyanine photography are given in table 2. Most of the lines are so very hazy and wide that capital initial letters are required to represent these characteristics.

TABLE 2.—*Arc spectrum of potassium*

Intensity	λ_{air} I.A.	ν_{vac} cm^{-1}	Term combination
15r	11, 773. 05	8, 491. 65	$4^2P^{\circ}_{1/2}$–$3^2D_{2/2}$
3	11, 769. 41	8, 494. 28	$4^2P^{\circ}_{1/2}$–$3^2D_{1/2}$
10	11, 690. 17	8, 551. 85	$4^2P^{\circ}_{1/2}$–$3^2D_{1/2}$
10HW	11, 022. 3	9, 070. 0	$3^2D_{1/2}$–5^2F°
			$3^2D_{2/2}$–5^2F°
1H	10, 487. 7	9, 532. 3	$3^2D_{1/2}$–$7^2P_{1/2}$
3H	10, 480. 3	9, 539. 0	$3^2D_{2/2}$–$7^2P^{\circ}_{1/2}$
10H	9, 955. 2	10, 042. 2	$5^2S_{1/2}$–$7^2P^{\circ}_{1/2}$
20H	9, 950. 5	10, 047. 0	$5^2S_{1/2}$–$7^2P^{\circ}_{1/2}$
20HlW	9, 597. 1	10, 417. 0	$3^2D_{1/2}$–6^2F°
50HlW	9, 591. 8	10, 422. 7	$3^2D_{2/2}$–6^2F°

(*d*) RUBIDIUM (Rb, Z=37)

Although the principal series of Rb begins with a widely separated term (237.6 cm^{-1}) no ^2P terms beyond the sixth and no ^2D or ^2F terms have been resolved. The second and third members of the fundamental series and two other doublet combinations in the infrared have now been photographed with xenocyanine plates. All of these lines are too hazy and unsymmetrical for precision measurements, but two of the pairs show separations of 19.3 cm^{-1} and, therefore, involve the 6^2P term. The fundamental series members are observed also as pairs (with separations of 20.6 and 10.5 cm^{-1}), but with very anomalous intensity ratios which suggest that the two main lines are fused. Furthermore, the satellites which ordinarily have the largest wave length here appear with shorter wave length and while all of these lines are usually shaded to longer waves, the satellite at 10,053 A is unexpectedly shaded toward the violet. These peculiarities are illustrated in figure 1 and in table 3.

TABLE 3.—*Arc spectrum of rubidium*

Intensity	λ_{air} IA.	ν_{vac} cm^{-1}	Term combination
2Hl	10, 305. 3	9, 701. 1	$6^2S_{1/2}$ –$8^2P^{\circ}_{1/2}$
4Hl	10, 284. 8	9, 720. 4	$6^2S_{1/2}$ –$8^2P^{\circ}_{1/2}$
500 Hl	10, 076. 1	9, 921. 8	4^2D –5^2F°
30Hv	10, 055. 2	9, 942. 4	4^2D –5^2F°
5Hl	9, 540. 8	10, 478. 4	$4^2D_{1/2}$–$8^2P^{\circ}_{1/2}$
10Hl	9, 523. 4	10, 497. 6	$4^2D_{2/2}$–$8^2P^{\circ}_{1/2}$
100 Hl	8, 869. 7	11, 271. 2	4^2D –6^2F°
20 Hl	8, 861. 5	11, 281. 7	4^2D –6^2F°

(*e*) CESIUM (Cs, Z=55)

In the arc spectrum of Cs Fowler lists the separations of nine successive ^2P terms and of five terms in the ^2D sequence. The ^2F terms were not resolved until Meissner [5] examined the vacuum arc spectrum of Cs with a Fabry-Perot interferometer and found satellites close to

[5] K. W. Meissner, Ann. d. Phys., vol. 65, p. 378, 1921.

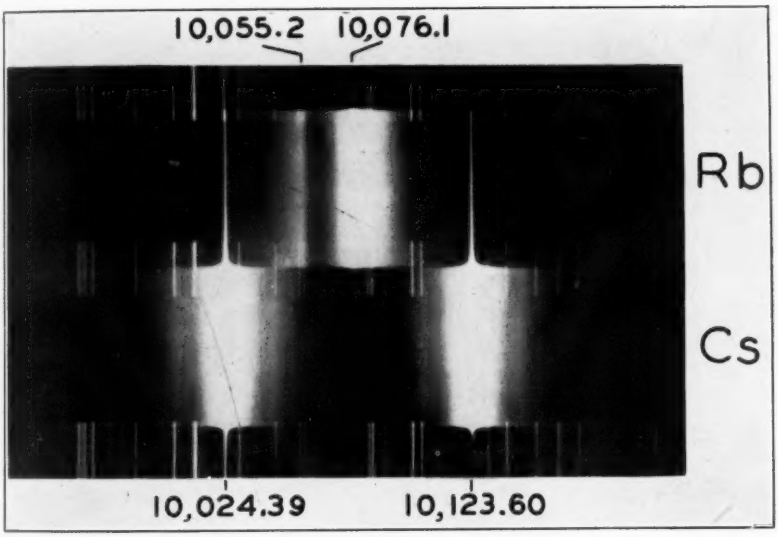


FIGURE 1.—*Fundamental series lines in arc spectra of rubidium and cesium.*

UNIV. OF MICH.

the stronger lines of longer wave length, but on the violet side. Data for the second member of the fundamental series are as follows:

Combination	Intensity	Wave length A	Separation cm^{-1}	
$^2D_{2½}$–$^2F^3_{3½}$	10	8, 079. 021		
$^2D_{2½}$–$^2F^2_{2½}$	2	8, 078. 923	97. 59	97. 74
$^2D_{1½}$–$^2F^2_{2½}$	10	8, 015. 710		

This shows that the F terms for Cs are very narrow doublets, and furthermore that they are inverted so that the lower energy level has the larger j value.

The arc spectrum of cesium is the only one in which the first lines of the fundamental series are within easy reach of the xenocyanine plate. It is also the first alkali spectrum in which lines of this type become sharp enough to observe reasonably well in the ordinary arc. A reproduction of the lines beyond 10,000 A is shown in figure 1. The two Cs lines appear to be about equal in intensity, but if allowance is made for the gradual decline in photographic sensitivity, the line of greater wave length must be judged the more intense. The theoretical intensity ratio is 21 to 14 if the intensity of the satellite (1) is added to that of the stronger component (20). Data for infrared lines of Cs photographed with xenocyanine are presented in table 4. The observed separation of the fundamental series doublet (97.73 cm^{-1}) is in excellent agreement with the value (97.74 cm^{-1}) found by Meissner between the main lines of the second member.

TABLE 4.—*Arc spectrum of cesium*

Intensity	λ_{air} I.A.	ν_{vac} cm^{-1}	Term combination
1,200	10, 123. 60	9, 875. 20	$5^2D_{2½}$–$4^2F^3_{3½}$
1,000	10, 024. 39	9, 972. 93	$5^2D_{1½}$–$4^2F^3_{3½}$
200	9, 208. 46	10, 856. 60	$6^2P^3_{1½}$–$6^2D_{1½}$
1,000	9, 172. 24	10, 899. 48	$6^2P^3_{1½}$–$6^2D_{2½}$
2,000 R	8, 943. 50	11, 178. 24	$6^2S_{½}$–$6^2P^2_{½}$
500	8, 761. 38	11, 410. 60	$6^2P^2_{½}$–$6^2D_{1½}$
4,000 R	8, 521. 10	11, 732. 35	$6^2S_{½}$–$6^2P^3_{1½}$

2. ALKALINE EARTHS

Compared with the simple doublet spectra of alkali atoms the presence of two valence electrons in alkaline earth (or earth) atoms produces very similar types of spectral series except that the multiplicities are odd, and two complete sets of terms appear, one set belonging to the singlet and the other to the triplet system. When alkaline earth atoms are singly ionized, so that only one valence electron remains, the atoms again exhibit doublet spectra like the neutral alkalis, but the corresponding lines are displaced toward higher frequencies. The published information on the structural analyses of alkaline earth spectra will be found in the treatises referred to above.[6] New terms reported by Russell and Saunders[7] accounted for practi-

[6] See footnote 5, p. 672.
[7] H. N. Russell and F. A. Saunders, Astrophys. J. vol. 61, p. 38, 1925.

cally all of the stronger lines of Ca, Sr, and Ba, and contained a clue to the interpretation of complex spectra characteristic of atoms with two or more valence electrons. Professor Russell has still farther extended the analysis of these spectra and has kindly communicated new or revised term values with permission to use them in the interpretation of the data in this paper.

It is unfortunate that almost nothing is known of the arc spectrum of the heaviest alkaline earth—radium. Cooperation of a radium chemist and a spectroscopist could remedy this defect with little or no loss of precious material.

(a) CALCIUM (Ca, Z=20)

Exploration of the infrared arc spectrum of Ca with xenocyanine plates has yielded some new results, including a $^3P^o$–^3P multiplet (10,833 to 10,880 A) and a new system of band heads. The band spectrum of CaO in the red and adjacent infrared has been studied recently by Brodersen [8] who measured 20 band heads, arranged them all in a single system, in which both electron terms are $^1\Sigma$, and analyzed the rotation structure of three of them (7,308, 7,318, and 8,652 A). Most of these bands were also recognized on my spectrograms, although many of them are faint and lack the characteristic aspect of band heads. The vibrational analysis of these bands (system I) is displayed in table 5. Several new sequences of band heads were recorded farther in the infrared; the intervals between their vibration levels are not identifiable with those of system I, so they are arranged and presented as system II in table 5.

All the data obtained from my Ca spectrograms are collected in table 6, and the Ca I spectral terms involved in the production of red and infrared lines are shown in table 7. In this, and in succeeding tables, the letters *n*, *p*, symbolize band head and part of band, respectively.

TABLE 5.—*CaO bands*

SYSTEM I

v' \ v''	0	1	2	3	4	5
0	7, 308. 31(2) 13, 679. 29 *692. 48*		8, 152. 96(40) 12, 262. 12 *694. 8* *695. 00*	8, 642. 7(2) 11, 567. 3 *694. 8*		
1	6, 956. 18(20) 14, 371. 75 *711. 3*	7, 318. 4(3) 13, 660. 4 *703. 2* *686. 1*	7, 715. 59(5) 12, 957. 21 *695. 1* *686. 1*	8, 152. 96(40) 12, 262. 12 *707. 5* *685. 9*	8, 652. 16(20) 11, 554. 64 *686. 1*	
2		6, 968. 4(2) 14, 346. 5 *703. 2*	7, 327. 6(2) 13, 643. 3 *695. 3* *673. 5*	7, 721. 1(4) 12, 948. 0 *707. 3*	8, 167. 2(5) 12, 240. 7 *656. 1*	8, 629. 8(1) 11, 584. 6
3			6, 982. 9(3) 14, 316. 8			

[8] P. H. Brodersen, Zeitschr. f. Phys. vol. 79, p. 613, 1932.

TABLE 5.—*CaO bands*—Continued

SYSTEM II

v'' \ v'	0	1	2	3	4	5
0	10, 533. 6(3) 9, 490. 8 *674. 5*	(8, 853)				
1	9, 834. 7(30) 10, 165. 3 *636. 4* *667. 3*	10, 491. 5(4) 9, 528. 9 *684. 8*	(8, 907)			
2	9, 228. 9(20) 10, 832. 6 *638. 9* *655. 1*	9, 807. 3(20) 10, 193. 7 *622. 1* *655. 8*	10, 444. 7(5) 9, 571. 6	(8, 960)		
3		9, 215. 1(5) 10, 848. 8 *621. 4*	9, 775. 0(15) 10, 227. 4 *611. 6* *647. 0*	10, 396. 7(6) 9, 615. 8 *647. 8*	(9, 021)	
4			9, 193. 4(2) 10, 874. 4 *611. 5*	9, 741. 0(5) 10, 263. 1 *595. 4*	10, 339. 8(5) 9, 668. 7 *657. 8*	(9, 078)
5					9, 700. 0(10) 10, 306. 5 *590. 5*	10, 289. 5(5) 9, 716. 0

TABLE 6.—*Arc spectrum of calcium*

Intensity	λ_{air} I. A.	ν_{vac} cm^{-1}	Term combination
4	10, 879. 78	9, 188. 85	$dp\,^3P_1^\circ$–$d^2\,^3P_0$
3	10, 869. 37	9, 197. 65	$dp\,^3P_2^\circ$–$d^2\,^3P_1$
2	10, 863. 72	9, 202. 43	$dp\,^3P_1^\circ$–$d^2\,^3P_1$
3	10, 861. 51	9, 204. 31	$dp\,^3P_0^\circ$–$d^2\,^3P_1$
10	10, 838. 77	9, 223. 61	$dp\,^3P_2^\circ$–$d^2\,^3P_2$
4	10, 833. 12	9, 228. 43	$dp\,^3P_1^\circ$–$d^2\,^3P_2$
3nl	10, 533. 6	9, 490. 8	II 0, 0
4nl	10, 491. 5	9, 528. 9	II 1, 1
5nl	10, 444. 7	9, 571. 6	II 2, 2
6nl	10, 396. 7	9, 615. 8	II 3, 3
500	10, 343. 85	9, 664. 93	$4\,^1P_1^\circ$–$5\,^1S_0$
5n?	10, 339. 8	9, 668. 7	II 4, 4
5n?	10, 289. 5	9, 716. 0	II 5, 5
30nl	9, 834. 7	10, 165. 3	II 1, 0
20nl	9, 807. 3	10, 193. 7	II 2, 1
15nl	9, 775. 0	10, 227. 4	II 3, 2
5n?	9, 741. 0	10, 263. 1	II 4, 3
20	9, 701. 7	10, 304. 6	$dp\,^3D_3^\circ$–$d^2\,^3P_2$
10n?	9, 700. 0	10, 306. 5	II 5, 4
15	9, 688. 6	10, 318. 6	$dp\,^3D_2^\circ$–$d^2\,^3P_1$
5	9, 676. 0	10, 332. 0	$dp\,^3D_1^\circ$–$d^2\,^3P_0$
5p?	9, 664. 0	10, 344. 8	$dp\,^3D_2^\circ$–$d^2\,^3P_2$
20p?	9, 233. 4	10, 827. 3	
20nl	9, 228. 9	10, 832. 6	II 2, 0
5nl	9, 215. 1	10, 848. 8	II 3, 1

TABLE 6.—*Arc spectrum of calcium*—Continued

Intensity	λ_{air} I. A.	ν_{vac} cm^{-1}	Term combination
2p?	9, 193. 4	10, 874. 4	II 4, 2
1, 000	8, 662. 16	11, 541. 30	$3^3D_{1\frac{1}{2}}$–$4^3P^\circ_{\frac{1}{2}}$
20nl	8, 652. 16	11, 554. 64	I 1, 4
2nl	8, 642. 7	11, 567. 3	I 0, 3
1nl	8, 629. 8	11, 584. 6	I 2, 5
1, 500	8, 542. 11	11, 703. 50	$3^3D_{2\frac{1}{2}}$–$4^3P^\circ_{1\frac{1}{2}}$
300	8, 498. 03	11, 764. 20	$3^3D_{1\frac{1}{2}}$–$4^3P^\circ_{1\frac{1}{2}}$
5	8, 169. 8	12, 236. 8	$dp^3P^\circ_1$–$d.d^3S_1$
5p?	8, 167. 2	12, 240. 7	I 2, 4
40nl	8, 152. 96	12, 262. 12	I 0, 2 I 1, 3
3	8, 005. 26	12, 488. 36	
4p?	7, 721. 1	12, 948. 0	I 2, 3
5nl	7, 715. 59	12, 957. 21	I 1, 2
2p?	7, 327. 6	13, 643. 3	I 2, 2
400	7, 326. 11	13, 646. 06	$4^1P^\circ_1$–4^1D_2
3nl	7, 318. 4	13, 660. 4	I 1, 1
2nl	7, 308. 31	13, 679. 29	I 0, 0
200	7, 203. 17	13, 880. 89	3^1D_2–$dp^3F^\circ_2$
500	7, 148. 12	13, 985. 84	3^1D_2–$dp^1D^\circ_2$
3nl	6, 982. 9	14, 316. 8	I 3, 2
2p?	6, 968. 4	14, 346. 5	I 2, 1
20nl	6, 956. 18	14, 371. 75	I 1, 0
6h	6, 798. 51	14, 705. 05	3^1D_2–$5^3P^\circ_1$
5h	6, 784. 01	14, 736. 48	
500h	6, 717. 75	14, 881. 84	3^1D_2–$dp^1P^\circ_1$
50	6, 572. 76	15, 210. 12	4^1S_0–4^3P_1

TABLE 7.—*Ca I spectral terms*

Even				Odd			
Singlets		Triplets		Singlets		Triplets	
Symbol	Value	Symbol	Value	Symbol	Value	Symbol	Value
4^1S_0	49, 304. 80	$d^2\ ^3F_2$	3, 347. 3	$4^1P^\circ_1$	25, 652. 49	$4^3P^\circ_0$	34, 146. 90
3^1D_2	27, 455. 59	$d^2\ ^3F_3$	3, 292. 7	$dp^1D^\circ_2$	13, 469. 77	$4^3P^\circ_1$	34, 094. 74
5^1S_0	15, 988. 2	$d^2\ ^3F_4$	3, 243. 0	$dp^1P^\circ_1$	12, 573. 62	$4^3P^\circ_2$	33, 988. 88
4^1D_2	12, 006. 41	$d^2\ ^3P_0$	780. 70			$dp^3F^\circ_2$	13, 574. 72
		$d^2\ ^3P_1$	767. 18			$dp^3F^\circ_3$	13, 486. 45
		$d^2\ ^3P_2$	741. 23			$dp^3F^\circ_4$	13, 408. 31
		$d.d^3D_1$	−2, 046. 84			$5^3P^\circ_0$	12, 757. 46
		$d.d^3D_2$	−2, 065. 77			$5^3P^\circ_1$	12, 750. 38
		$d.d^3D_3$	−2, 091. 30			$5^3P^\circ_2$	12, 730. 13
		$d.d^3S_1$	−2, 266. 40			$dp^3D^\circ_1$	11, 112. 76
						$dp^3D^\circ_2$	11, 086. 03
						$dp^3D^\circ_3$	11, 046. 02
						$dp^3P^\circ_0$	9, 971. 73
						$dp^3P^\circ_1$	9, 969. 82
						$dp^3P^\circ_2$	9, 965. 05

(*b*) STRONTIUM (Sr, Z=38)

The most prominent feature of the infrared arc spectrum of Sr is the $^2D-{}^2P$ multiplet characteristic of singly ionized Sr atoms. Oxide bands which are so prominent and disturbing in the Ca I spectrum are also strongly developed in the Sr arc at atmospheric pressure, but their number is insufficient for a vibrational analysis. Results from Sr spectrograms in the red and infrared are presented in table 8 and the Sr I spectral terms used here are listed in table 9.

TABLE 8.—*Arc spectrum of strontium*

Intensity	λ_{air} I.A.	ν_{vac} cm^{-1}	Term combination
5	11, 241. 32	8, 893. 32	$5^1P_1^\circ-6^1S_0$
200	10, 914. 83	9, 159. 34	$4^3D_{1\frac{1}{2}}-5^3P_{1}^\circ$
5nl	10, 437. 1	9, 578. 6	
2nl	10, 426. 2	9, 588. 6	
1, 000	10, 327. 29	9, 680. 43	$4^3D_{2\frac{1}{2}}-5^3P_{1\frac{1}{2}}^\circ$
300	10, 036. 59	9, 960. 81	$4^3D_{1\frac{1}{2}}-5^3P_{1\frac{1}{2}}^\circ$
20nl	9, 776. 26	10, 226. 06	
10nl	9, 196. 08	10, 871. 2	
10nl	8, 700. 05	11, 491. 1	
5nl	8, 257. 78	12, 106. 47	
3nl	7, 882. 36	12, 683. 07	
200hv	7, 673. 06	13, 029. 03	$5^1P_1^\circ-5^1D_2$
100	7, 621. 50	13, 117. 17	$4^1D_2-dp^3F_2^\circ$
1	7, 503. 38	13, 323. 66	$5^1P_1^\circ-5^3D_2$
3	7, 438. 42	13, 440. 03	$4^1D_2-dp^3F_3^\circ$
5	7, 408. 12	13, 494. 99	$5^1P_1^\circ-p^2\,{}^3P_0$
500	7, 309. 41	13, 677. 23	$4^1D_2-dp^1D_2^\circ$
20h	7, 287. 41	13, 718. 52	$4^1D_2-6^3P_1^\circ$
100hl	7, 232. 20	13, 823. 25	$4^1D_2-6^3P_2^\circ$
200hl	7, 167. 20	13, 948. 61	$4^1D_2-6^1P_1^\circ$
30	7, 153. 02	13, 976. 26	$5^1P_1^\circ-p^2\,{}^3P_2$
2, 000	7, 070. 10	14, 140. 18	$5^3P_2^\circ-6^3S_1$
200	6, 892. 56	14, 504. 40	$5^1S_0-5^3P_1^\circ$
1, 000	6, 878. 32	14, 534. 43	$5^3P_1^\circ-6^3S_1$
500	6, 791. 00	14, 721. 32	$5^3P_0^\circ-6^3S_1$
200	6, 643. 53	15, 048. 09	$4^3D_2-dp^3F_2^\circ$
300	6, 617. 26	15, 107. 83	$4^3D_1-dp^3F_2^\circ$
200	6, 550. 22	15, 262. 45	$5^1P_1^\circ-p^2\,{}^1D_2$
50	6, 546. 77	15, 270. 50	$4^3D^3-dp^3F_3^\circ$

TABLE 9.—*Sr I spectral terms*

Even				Odd			
Singlets		Triplets		Singlets		Triplets	
Symbol	Value	Symbol	Value	Symbol	Value	Symbol	Value
5^1S_0	45, 925. 6	4^3D_1	27, 766. 83	$5^1P_1^\circ$	24, 227. 16	$5^3P_0^\circ$	31, 608. 0
4^1D_2	25, 776. 13	4^3D_2	27, 707. 06	$dp\,^1D_2^\circ$	12, 098. 97	$5^3P_1^\circ$	31, 421. 1
6^1S_0	15, 337. 8	4^3D_3	27, 606. 49	$6^1P_1^\circ$	11, 827. 62	$5^3P_2^\circ$	31, 026. 8
5^1D_2	11, 198. 1	6^3S_1	16, 886. 8			$dp^3F_2^\circ$	12, 658. 99
$p^2\ ^1D_2$	8, 964. 6	5^3D_1	10, 918. 3			$dp^3F_3^\circ$	12, 336. 08
		5^3D_2	10, 903. 3			$dp^3F_4^\circ$	12, 006. 44
		5^3D_3	10, 880. 5			$6^3P_0^\circ$	12, 072. 47
		$p^2\ ^3P_0$	10, 731. 8			$6^3P_1^\circ$	12, 057. 62
		$p^2\ ^3P_1$	10, 525. 5			$6^3P_2^\circ$	11, 952. 83
		$p^2\ ^3P_2$	10, 250. 7				

(c) BARIUM (Ba, Z=56)

The red and infrared arc spectrum of Ba is characterized by a relatively large number of Ba I lines, but the bands associated with oxides are almost absent, and no trace of Ba II lines is found. Results for 150 Ba I lines are displayed in table 10. Nearly all of these lines are accounted for as combinations of Ba I spectral terms shown in table 11.

TABLE 10.—*Arc spectrum of barium*

Intensity	λ_{air} I. A.	ν_{vac} cm^{-1}	Term combination
2h	11, 114. 3	8, 994. 96	$dp^3D_2^\circ$–$d.s^3D_3$
2h	11, 012. 7	9, 077. 94	$dp^1F_3^\circ$–$d.d^3G_3$
1	10, 962. 6	9, 119. 43	$dp^3P_1^\circ$–$p^2\ ^3P_1$
3h	10, 888. 6	9, 181. 40	$dp^3P_0^\circ$–$p^2\ ^3P_1$
5h	10, 791. 24	9, 264. 24	$dp^3D_2^\circ$–$d.s^1D_2$
1h	10, 769. 3	9, 283. 11	
5h	10, 693. 7	9, 348. 74	$dp^1F_3^\circ$–$d.d^1F_3$
10	10, 649. 07	9, 387. 92	$dp^3P_2^\circ$–$p^2\ ^1D_2$
5	10, 540. 04	9, 485. 03	
2h	10, 487. 3	9, 532. 73	$dp^1F_3^\circ$–$d.d^3G_4$
100	10, 471. 26	9, 547. 33	$6^3P_2^\circ$–$d^2\ ^1D_2$
2h	10, 409. 6	9, 603. 89	$dp^3D_1^\circ$–$d.s^1D_2$
10h	10, 370. 34	9, 640. 25	$dp^3P_1^\circ$–$p^2\ ^1D_2$
8hl	10, 349. 03	9, 660. 10	$dp^3P_2^\circ$–$p^2\ ^3P_2$
50hl	10, 274. 04	9, 730. 61	$dp^1D_2^\circ$–$d.s^3D_1$
400hl	10, 233. 22	9, 769. 42	$dp^3F_4^\circ$–$d.s^3D_3$
50h	10, 188. 23	9, 812. 56	$dp^1F_3^\circ$–$d.d^3D_3$
10	10, 129. 68	9, 869. 28	$dp^1D_2^\circ$–$d.s^3D_2$
5h	10, 115. 14	9, 883. 46	
2h	10, 085. 42	9, 912. 59	$dp^3P_1^\circ$–$p^2\ ^3P_2$
200	10, 032. 12	9, 965. 25	$6^3P_2^\circ$–$d^2\ ^3P_1$
300	10, 001. 09	9, 996. 17	$dp^3F_3^\circ$–$d.s^3D_2$
500hl	9, 830. 37	10, 169. 77	$6^1P_1^\circ$–7^1S_0
3h	9, 821. 60	10, 178. 85	$dp^3D_1^\circ$–$p^2\ ^1S_0$
5h	9, 792. 91	10, 208. 67	$dp^3P_2^\circ$–$d.d^1F_3$

TABLE 10.—*Arc spectrum of barium*—Continued

Intensity	λ_{air} I. A.	ν_{vac} cm^{-1}	Term combination
6h	9, 772. 62	10, 229. 87	$dp\,^3P_1^\circ - d.d\,^3D_1$
2h	9, 759. 35	10, 243. 78	$dp\,^3P_2^\circ - d.d\,^3D_2$
60	9, 713. 75	10, 291. 86	$dp\,^3P_0^\circ - d.d\,^3D_1$ $dp\,^3D_2^\circ - p^2\,^3P_1$
20h	9, 704. 42	10, 301. 76	$dp\,^3D_1^\circ - p^2\,^3P_0$
10nl	9, 658. 8	10, 350. 4	
100h	9, 645. 72	10, 364. 45	$dp\,^3D_3^\circ - p^2\,^1D_2$
300	9, 608. 88	10, 404. 19	$6^3P_2^\circ - d^2\,^3P_2$
150	9, 589. 37	10, 425. 36	$6^3P_2^\circ - d^2\,^1D_2$
10h	9, 530. 30	10, 489. 97	$dp\,^3P_2^\circ - d.d\,^3S_1$
60h	9, 524. 70	10, 496. 14	$dp\,^3P_1^\circ - d.d\,^3D_2$
100	9, 455. 92	10, 572. 49	$6^3P_1^\circ - d^2\,^3P_0$
15h	9, 450. 05	10, 579. 05	$dp\,^3F_3^\circ - d.s\,^3D_3$
4h	9, 414. 6	10, 618. 9	$dp\,^1F_3^\circ - 8^1D_2$
10	9, 403. 53	10, 631. 39	$dp\,^3D_1^\circ - p^2\,^3P_1$
6h	9, 398. 8	10, 636. 7	$dp\,^3D_3^\circ - p^2\,^3P_2$
500	9, 370. 06	10, 669. 37	$5^1D_2 - dp\,^3F_2^\circ$
80h	9, 367. 45	10, 672. 34	$dp\,^3P_2^\circ - d.d\,^3D_3$
100h	9, 324. 58	10, 721. 40	$dp\,^1D_2^\circ - d.s\,^1D_2$
100	9, 308. 08	10, 740. 41	$dp\,^3F_2^\circ - d.s\,^3D_1$
10	9, 306. 52	10, 742. 21	$dp\,^3P_1^\circ - d.d\,^3S_1$
15h	9, 253. 08	10, 804. 25	$dp\,^3P_0^\circ - d.d\,^3S_1$
1h	9, 245. 6	10, 813. 0	$dp\,^3D_2^\circ - p^2\,^1D_2$
100	9, 219. 69	10, 843. 38	$6^3P_1^\circ - d^2\,^3P_1$
15h	9, 215. 42	10, 848. 40	$dp\,^3F_3^\circ - d.s\,^1D_2$
60h	9, 189. 57	10, 878. 92	$dp\,^3F_2^\circ - d.s\,^3D_2$
10h	9, 159. 66	10, 914. 44	$dp\,^3D_3^\circ - d.d\,^3G_3$
15h	9, 133. 29	10, 945. 95	$dp\,^3P_2^\circ - d.d\,^1P_1$
3ln	9, 101. 7	10, 983. 9	
2h	9, 097. 8	10, 988. 7	
3h	9, 018. 63	11, 085. 12	$dp\,^3D_2^\circ - p^2\,^3P_2$
2h	8, 975. 6	11, 138. 3	
10h	8, 937. 93	11, 185. 20	$dp\,^3D_3^\circ - d.d\,^1F_3$
7hl	8, 927. 41	11, 198. 39	$dp\,^3P_1^\circ - d.d\,^1P_1$
150	8, 914. 99	11, 213. 99	$6^3P_0^\circ - d^2\,^3P_1$
3h	8, 909. 83	11, 220. 48	$dp\,^3D_3^\circ - d.d\,^3D_2$
100	8, 860. 98	11, 282. 33	$6^3P_1^\circ - d^2\,^3P_2$
100h	8, 799. 76	11, 360. 83	$dp\,^1F_3^\circ - d.d\,^1G_4$
3h	8, 793. 36	11, 369. 10	$dp\,^3D_3^\circ - d.d\,^3G_4$
1h	8, 767. 7	11, 402. 4	$dp\,^3D_2^\circ - d.d\,^3D_1$
3h	8, 737. 74	11, 441. 47	
3h	8, 710. 82	11, 476. 83	
60	8, 654. 07	11, 552. 09	$5^1D_2 - dp\,^3F_3^\circ$
4hl	8, 593. 48	11, 633. 54	$dp\,^3D_2^\circ - d.d\,^1F_3$
50hl	8, 581. 98	11, 649. 13	$dp\,^3D_3^\circ - d.d\,^3D_3$
40hl	8, 567. 58	11, 668. 70	$dp\,^3D_2^\circ - d.d\,^3D_2$
600h	8, 559. 97	11, 679. 08	$5^1D_2 - d.p\,^1D_2^\circ$
8hl	8, 521. 96	11, 731. 17	$dp\,^3F_2^\circ - d.s\,^1D_2$
30hl	8, 514. 23	11, 741. 82	$dp\,^3D_1^\circ - d.d\,^3D_1$
4hv	8, 414. 58	11, 880. 87	$dp\,^3P_2^\circ - d.d\,^1D_2$
2h	8, 350. 76	11, 971. 67	$dp\,^3P_1^\circ - d.d\,^3P_0$

TABLE 10.—*Arc spectrum of barium*—Continued

Intensity	λ_{air} I. A.	ν_{vac} cm^{-1}	Term combination
20h	8, 325. 38	12, 008. 27	$dp^3D_1^1$–$d.d^3D_2$
6hv	8, 285. 00	12, 066. 69	$dp^3P_2^2$–$d.d^3P_1$
3h	8, 264. 01	12, 097. 34	$dp^3D_2^2$–$d.d^3D_3$
5h	8, 224. 41	12, 155. 59	
300h	8, 210. 30	12, 176. 48	$6^1P_1^1$–6^1D_2
10hl	8, 161. 58	12, 249. 17	
3h	8, 158. 12	12, 254. 36	$dp^3D_1^1$–$d.d^3S_1$
30h	8, 147. 78	12, 269. 91	$dp^1D_2^2$–$p^2\ ^1D_2$
30hv	8, 120. 49	12, 311. 15	$dp^3P_2^2$–$d.d^3P_2$
1h	8, 074. 58	12, 381. 14	$dp^3P_0^2$–$d.d^3P_1$
10	8, 018. 23	12, 468. 16	5^3D_3–$dp^3F_2^3$
15hv	7, 982. 40	12, 524. 12	$dp^3D_3^3$–$d.d^3F_3$
10hv	7, 961. 24	12, 557. 41	$dp^3D_2^3$–$d.d^3F_2$
2h	7, 957. 33	12, 563. 58	$dp^3P_1^1$–$d.d^3P_2$
3h	7, 939. 42	12, 591. 92	$dp^3F_4^4$–$d.d^3G_4$
200	7, 911. 31	12, 636. 66	6^1S_0–6^3P_1
500	7, 905. 77	12, 645. 51	$6^3P_2^2$–7^3S_1
20hl	7, 877. 93	12, 690. 20	$6^1P_1^1$–6^3D_2
1h	7, 865. 29	12, 710. 60	$dp^3D_1^1$–$d.d^1P_1$
60h	7, 839. 52	12, 752. 38	$dp^3D_3^3$–$d.d^3F_4$
5h	7, 798. 26	12, 819. 85	$dp^1D_2^2$–$d.d^3G_3$
400	7, 780. 46	12, 849. 18	5^3D_2–$dp^3F_2^2$
10h	7, 775. 37	12, 857. 59	$dp^3D_3^3$–$d.d^1D_2$
10hl	7, 766. 80	12, 871. 78	$dp^3F_4^4$–$d.d^3D_3$
40hv	7, 751. 68	12, 896. 88	$dp^3D_1^1$–$d.d^3F_2$
10h	7, 721. 78	12, 946. 82	$dp^3F_3^3$–$d.d^3G_3$
50hv	7, 706. 51	12, 972. 48	$dp^3D_2^3$–$d.d^3F_3$
600	7, 672. 06	13, 030. 73	5^3D_1–$dp^3F_2^2$
200hl	7, 642. 91	13, 080. 42	$dp^3F_4^4$–$d.d^3G_5$
150hl	7, 636. 90	13, 090. 72	$dp^1D_2^2$–$d.d^1F_3$
50	7, 610. 45	13, 136. 22	5^1D_2–$dp^3D_2^2$
2h	7, 575. 22	13, 197. 31	$dp^3D_3^3$–$d.d^1G_4$
25h	7, 543. 48	13, 252. 84	$dp^3F_3^3$–$d.d^3D_2$
20h	7, 528. 20	13, 279. 73	$dp^3F_2^2$–$p^2\ ^1D_2$
20h	7, 523. 60	13, 287. 85	$dp^3D_3^3$–$d.d^3P_2$
3h	7, 513. 40	13, 305. 89	$dp^3D_2^3$–$d.d^1D_2$
200	7, 488. 04	13, 350. 96	5^3D_3–$dp^3F_3^3$
30h	7, 476. 21	13, 372. 08	$dp^1D_2^2$–$d.d^3S_1$
300hl	7, 459. 78	13, 401. 54	$dp^3F_3^3$–$d.d^3G_4$
100	7, 417. 48	13, 477. 96	5^3D_3–$dp^1D_2^2$
4hl	7, 414. 26	13, 483. 81	$dp^3D_1^1$–$d.d^3P_0$
30hv	7, 409. 97	13, 491. 62	$dp^3D_2^2$–$d.d^3P_1$
400	7, 392. 42	13, 523. 65	$6^3P_1^1$–7^3S_1
50hl	7, 375. 59	13, 554. 50	$dp^1D_2^2$–$d.d^3D_3$
20	7, 359. 29	13, 584. 53	5^1D_2–$dp^3D_3^3$
4h	7, 339. 57	13, 621. 03	$d^2\ ^3P_2$–$dp^3D_3^3$
10h	7, 326. 50	13, 645. 33	$dp^3D_1^1$–$d.d^1D_2$
10h	7, 307. 23	13, 681. 31	$dp^3F_3^3$–$d.d^3D_3$
5h	7, 304. 46	13, 686. 50	
1, 000	7, 280. 29	13, 731. 94	5^3D_2–$dp^3F_3^3$

TABLE 10.—*Arc spectrum of barium*—Continued

Intensity	λ_{air} I. A.	ν_{vac} cm^{-1}	Term combination
2h	7, 272. 33	13, 746. 97	$dp^3F_4^4$–$d.d^3F_3$
200hl	7, 228. 84	13, 829. 67	$dp^3F_3^3$–$d.d^3G_3$
10	7, 213. 56	13, 858. 97	5^3D_2–$dp^1D_2^2$
20h	7, 208. 18	13, 869. 31	$dp^3F_2^2$–$d.d^3D_1$
200	7, 195. 22	13, 894. 29	$6^3P_0^0$–7^3S_1
80hv	7, 153. 54	13, 975. 25	$dp^3F_4^4$–$d.d^3F_4$
4h	7, 133. 16	14, 015. 17	
10h	7, 126. 60	14, 028. 08	
800hv	7, 120. 27	14, 040. 55	5^3D_1–$dp^1D_2^2$
100hl	7, 090. 01	14, 100. 47	$dp^3F_2^3$–$d.d^1F_3$
1h	7, 072. 38	14, 135. 62	$dp^3F_2^2$–$d.d^3D_2$
3	7, 069. 43	14, 141. 52	$dp^3F_3^3$–$d.d^3F_2$
2, 000	7, 059. 92	14, 160. 57	5^3D_3–$dp^3F_4^4$
5	6, 986. 79	14, 308. 78	5^1D_2–$dp^3P_1^1$
2h	6, 961. 63	14, 360. 50	$dp^1D_2^2$–8^1D_2
2h	6, 932. 92	14, 419. 96	$dp^3F_4^4$–$d.d^1G_4$
100h	6, 867. 85	14, 556. 59	$dp^3F_3^3$–$d.d^3F_3$
200	6, 865. 67	14, 561. 21	5^1D_2–$dp^3P_2^2$
60h	6, 771. 85	14, 762. 95	$dp^1D_2^2$–$d.d^1D_2$
2h	6, 761. 86	14, 784. 76	$dp^3F_3^3$–$d.d^3F_4$
2h	6, 714. 03	14, 890. 08	$dp^3F_3^3$–$d.d^1D_2$
600	6, 693. 82	14, 935. 04	5^3D_3–$dp^3D_2^2$
500	6, 675. 26	14, 976. 56	5^3D_3–$dp^3D_1^1$
50	6, 654. 05	15, 024. 30	$dp^3F_2^2$–$d.d^3F_2$
1, 000	6, 595. 32	15, 158. 09	5^3D_1–$dp^3D_1^1$
20h	6, 580. 73	15, 191. 70	
3h	6, 564. 33	15, 229. 65	$dp^3F_3^3$–$d.d^1G_4$

TABLE 11.—*Ba I spectral terms*

Even				Odd			
Singlets		Triplets		Singlets		Triplets	
Symbol	Value	Symbol	Value	Symbol	Value	Symbol	Value
6^1S_0	42, 029. 40	5^3D_1	32, 995. 53	6^1P_1	23, 969. 30	6^3P_0	29, 763. 43
5^1D_2	30, 634. 04	5^3D_2	32, 814. 07	dp^1D_2	18, 955. 06	6^3P_1	29, 392. 82
$d^2\ ^1D_2$	18, 967. 45	5^3D_3	32, 433. 03	dp^1F_3	15, 213. 27	6^3P_0	28, 514. 69
7^1S_0	13, 799. 52	$d^2\ ^3P_0$	18, 820. 36			dp^3F_2	19, 964. 83
6^1D_2	11, 792. 73	$d^2\ ^3P_1$	18, 549. 43			dp^3F_3	19, 082. 06
ds^1D_2	8, 233. 58	$d^2\ ^3P_2$	18, 110. 48			dp^3F_4	18, 272. 54
$p^2\ ^1S_0$	7, 658. 70	7^3S_1	15, 869. 22			dp^3D_1	17, 837. 50
$p^2\ ^1D_2$	6, 685. 16	6^3D_1	11, 334. 05			dp^3D_2	17, 498. 04
$d.d^1F_3$	5, 864. 32	6^3D_2	11, 279. 02			dp^3D_3	17, 049. 70
$d.d^1P_1$	5, 126. 95	6^3D_3	11, 211. 54			dp^3P_0	16, 387. 49
8^1D_2	4, 594. 45	$d.s^3D_1$	9, 224. 43			dp^3P_1	16, 325. 35
$d.d^1D_2$	4, 192. 08	$d.s^3D_2$	9, 085. 74			dp^3P_2	16, 073. 03
$d.d^1G_4$	3, 852. 48	$d.s^3D_3$	8, 503. 12			$d.p^3D_1$	5, 533. 75
$d.d^1S_0$	2, 843. 90	$p^2\ ^3P_0$	7, 535. 73			$d.p^3D_2$	4, 966. 22
		$p^2\ ^3P_1$	7, 206. 11			$d.p^3D_3$	4, 489. 38
		$p^2\ ^3P_2$	6, 412. 77				
		$d.d^3G_3$	6, 135. 18				
		$d.d^3G_4$	5, 680. 54				
		$d.d^3G_5$	5, 192. 13				
		$d.d^3D_1$	6, 095. 55				
		$d.d^3D_2$	5, 829. 22				
		$d.d^3D_3$	5, 400. 72				
		$d.d^3S_1$	5, 583. 06				
		$d.d^3F_2$	4, 940. 70				
		$d.d^3F_3$	4, 525. 69				
		$d.d^3F_4$	4, 297. 34				
		$d.d^3P_0$	4, 353. 77				
		$d.d^3P_1$	4, 006. 39				
		$d.d^3P_2$	3, 761. 80				

WASHINGTON, February 25, 1933.

THE DETERMINATION OF STRESSES FROM STRAINS ON THREE INTERSECTING GAGE LINES AND ITS APPLICATION TO ACTUAL TESTS

By Wm. R. Osgood and Rolland G. Sturm [1]

ABSTRACT

The paper presents a graphical construction for determining in problems of plane stress the state of strain at a point from measured strains taken on three gage lines intersecting at the point. The method is based on the dyadic circle, first used by Otto Mohr for determining moments of inertia, later applied by Robert Land to the plane state of stress, and finally generalized by H. M. Westergaard.

Applications of the method to various projects of the Aluminum Research Laboratories are noted, and examples of the use of the method in determining the state of strain in the end batten plate of a column are given.

CONTENTS

	Page
I. Theory	685
II. Applications to actual tests	691

I. THEORY

Not infrequently in cases of plane stress it is desired to determine the state of stress at a point from strains taken on short gage lines through the point. Usually the strains in such cases have been measured on four gage lines 45° apart, and the results interpreted, sometimes by cumbersome means. Although it is desirable where possible to take readings on four gage lines to obtain a check, only three gage lines are actually necessary. This obviates the necessity of preparing a fourth gage line, taking readings on it, and adjusting observations later, which in some cases may be inconvenient or impossible. The 3-gage-line method does not appear to be known widely—so far as the authors are aware, it has been disseminated primarily by Prof. H. M. Westergaard in his classes in the theory of elasticity. The only known published suggestion of the method appears in one of his papers,[2] but the application specifically to strains is not given there.

In the case of plane stress the equations expressing the relation between the components of strain at a point referred to any pair of rectangular axes, x' and y', parallel to the plane of stress and the components of the same strain referred to any other pair of rectangular axes, x and y, parallel to the plane of stress are [3]

$$\epsilon'_x=\frac{1}{2}(\epsilon_x+\epsilon_y)+\frac{1}{2}(\epsilon_x-\epsilon_y)\cos 2\psi+\frac{1}{2}\gamma \sin 2\psi \qquad (1)$$

[1] Research-engineer-physicist, Aluminum Co. of America, New Kensington, Pa.
[2] Anwendung der Statik auf die Augsleichungsrechnung, Göttingen, p. 37, 1925.
[3] Fuller and Johnston, Applied Mechanics, vol. 2, art. 42, John Wiley & Sons, New York. 1919 pp. 68, 69.

$$\epsilon'_y = \frac{1}{2}(\epsilon_x + \epsilon_y) - \frac{1}{2}(\epsilon_x - \epsilon_y)\cos 2\psi - \frac{1}{2}\gamma \sin 2\psi \tag{2}$$

$$\gamma' = (\epsilon_y - \epsilon_x)\sin 2\psi + \gamma \cos 2\psi \tag{3}$$

where

ϵ_x and ϵ_y are the components of strain in the directions x and y, respectively

γ is the shearing strain with respect to the axes of x and y

ψ is the angle measured positive counterclockwise from the positive axis of x to the positive axis of x'

ϵ'_x and ϵ'_y are the components of strain in the directions x' and y', respectively

and

γ' is the shearing strain with respect to the axes of x' and y'.

If now we know the strains ϵ_1, ϵ_2, ϵ_3 at a point in three directions making the angles ψ_1, ψ_2, ψ_3, respectively, with any axis x, as in figure 1(a), we may determine the state of strain at the point by the following construction:[4]

From any point T, as in figure 1 (b), lay off ϵ_1, ϵ_2, ϵ_3 in directions making angles $2\psi_1$, $2\psi_2$, $2\psi_3$, respectively, with the negative direction of the axis of x. A negative strain (a shortening) should be laid off from T in the opposite direction from that indicated; that is, making an angle $2\psi \pm \pi$ with the negative direction of the axis of x. (The strains laid off in figure 1 (b) are positive (elongations).) At the end points of ϵ_1, ϵ_2, ϵ_3 draw the three perpendiculars P_1, P_2, P_3, respectively, and in each case shade the side away from T if the corresponding strain is positive and toward T if the corresponding strain is negative. Now draw the circle which is tangent to the three perpendiculars either on all the shaded sides or on all the unshaded sides. (In general, it will be possible to draw four circles tangent to the three perpendiculars, but only one will satisfy the condition which has been imposed.) Through the center of the circle draw the axis Ox, and tangent to the circle the axis Oy, taking O so that the positive axis of x intersects the circle if the latter is tangent on the unshaded sides of P_1, P_2, P_3, and so that the negative axis of x intersects the circle if the latter is tangent on the shaded sides of P_1, P_2, P_3. The state of strain is determined completely by this construction.[5] For, from T drop the perpendicular TR on the axis of x. The strains ϵ_x, ϵ_y, and γ may be determined from the following three equations, obtained by substituting ϵ_1, ψ_1; ϵ_2, ψ_2; ϵ_3, ψ_3 in equation (1) three times successively

$$\epsilon_1 = \frac{1}{2}(\epsilon_x + \epsilon_y) + \frac{1}{2}(\epsilon_x - \epsilon_y)\cos 2\psi_1 + \frac{1}{2}\gamma \sin 2\psi_1$$

$$\epsilon_2 = \frac{1}{2}(\epsilon_x + \epsilon_y) + \frac{1}{2}(\epsilon_x - \epsilon_y)\cos 2\psi_2 + \frac{1}{2}\gamma \sin 2\psi_2$$

$$\epsilon_3 = \frac{1}{2}(\epsilon_x + \epsilon_y) + \frac{1}{2}(\epsilon_x - \epsilon_y)\cos 2\psi_3 + \frac{1}{2}\gamma \sin 2\psi_3.$$

[4] First used for determining moments of inertia by O. Mohr, Abhandlungen aus dem Gebiete der technischen Mechanik, 3d ed., p. 90, Wilhelm Ernst und Sohn, Berlin, 1928; later applied to the plane state of stress by Robt. Land, Zeitschrift des Vereines deutscher Ingenieure, vol. 39, p. 1551, Dec. 28, 1895.

[5] Professor Westergaard calls the circle here the "dyadic circle."

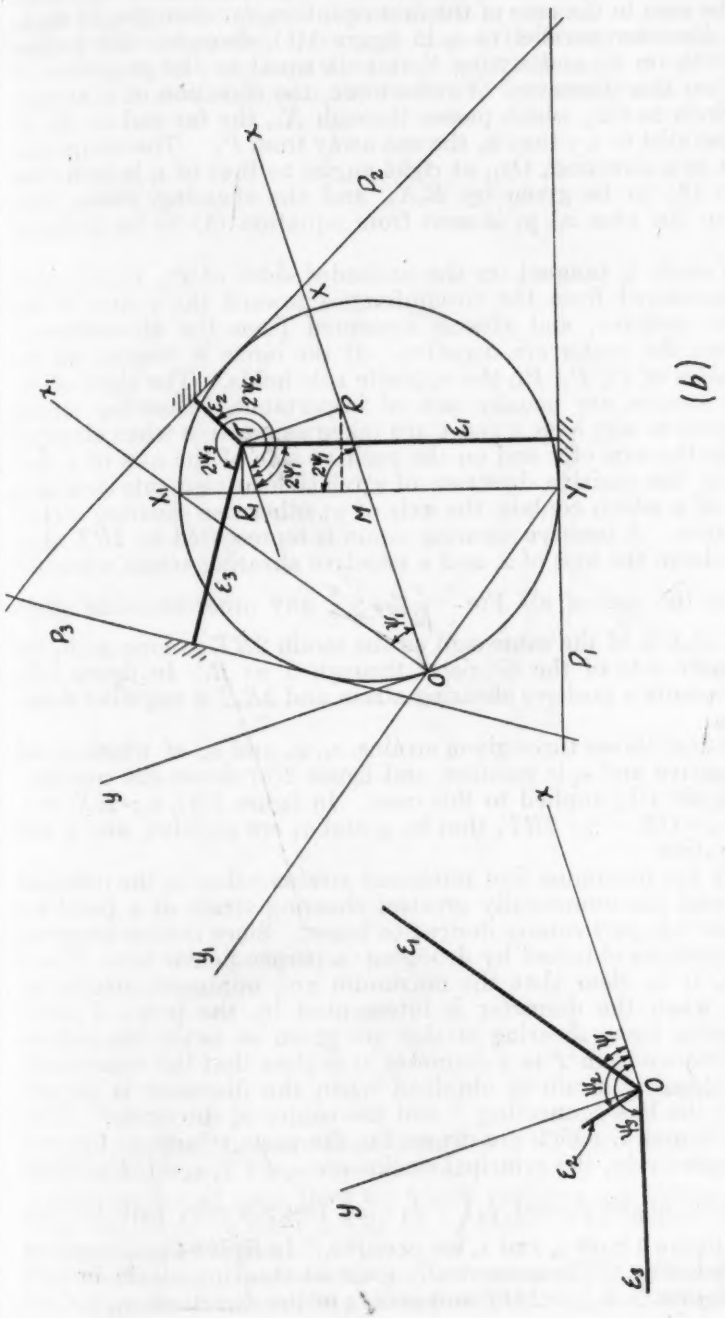


FIGURE 1.—*Three positive strains and the corresponding circle of strain.*

The values $\epsilon_x = OR$, $\epsilon_y = RX$, $\gamma = 2RT$ satisfy these three equations, as may be seen in the case of the first equation, for example, by drawing the diameter parallel to ϵ_1 in figure 1(*b*), dropping the perpendicular TR_1 on it, and noting that ϵ_1 is equal to the projection of Y_1MRT on this diameter. Furthermore, the direction of ϵ_1 appears in the circle as Ox_1, which passes through X_1, the far end of the diameter parallel to ϵ_1—that is, the end away from P_1. The component of strain in a direction, Oy_1, at right angles to that of ϵ_1 is seen from equation (2) to be given by R_1X_1, and the shearing strain with respect to the axes x_1, y_1 is seen from equation (3) to be given by $2R_1T$.

If the circle is tangent on the unshaded sides of P_1, P_2, P_3, then strains measured from the circumference toward the center of the circle are positive, and strains measured from the circumference away from the center are negative. If the circle is tangent on the shaded sides of P_1, P_2, P_3, the opposite rule holds. The signs of the shearing strains are usually not of importance. Shearing strains with respect to any axes x and y are taken as positive when elements normal to the axis of x and on the positive side of the axis of y tend to slide in the positive direction of y relative to elements normal to the axis of x which contain the axis of y; otherwise shearing strains are negative. A positive shearing strain is represented by $2RT$ when RT lies above the axis of x, and a negative shearing strain when RT lies below the axis of x. For $-\frac{\pi}{2} \leqq \psi \leqq \frac{\pi}{2}$ any other shearing strain such as $2R_1T$ is of the same sign as the strain $2RT$ so long as R_1 lies on the same side of the diameter through T as R. In figure 1(*b*), $2RT$ represents a positive shearing strain and $2R_1T$ a negative shearing strain.

Figure 2(*a*) shows three given strains, ϵ_1, ϵ_2, and ϵ_3, of which ϵ_1 and ϵ_3 are negative and ϵ_2 is positive, and figure 2(*b*) shows the construction of figure 1(*b*) applied to this case. In figure 2(*b*), $\epsilon_y = RX$, $\gamma_1 = 2R_1T$, $-\epsilon_x = OR$, $-\gamma = 2RT$; that is, ϵ_y and γ_1 are positive, and ϵ_x and γ are negative.

Usually the maximum and minimum strains—that is, the principal strains—and the numerically greatest shearing strain at a point are the strains it is particularly desired to know. Since strains are given as the intercepts obtained by dropping a perpendicular from T on a diameter, it is clear that the maximum and minimum strains are obtained when the diameter is intercepted by the point T itself. Furthermore, since shearing strains are given as twice the perpendicular distance from T to a diameter, it is clear that the numerically greatest shearing strain is obtained when the diameter is perpendicular to the line connecting T and the center of the circle.[6] Thus in figures 3 and 4, which are drawn for the same strains as figures 1 and 2, respectively, the principal strains are $\epsilon_u = VT$, $\epsilon_v = UT$ in directions making angles ψ_u and $\psi_v \left(= \psi_u + \frac{\pi}{2} \right)$, respectively, with the axis of x. In figure 3 both ϵ_u and ϵ_v are positive. In figure 4 ϵ_u is negative, and ϵ_v is positive. The numerically greatest shearing strain in each of these figures is $\gamma_{max} = 2MT$ and occurs in the directions x_s, y_s.

[6] It should be remembered that only conditions in one plane are being considered here, and that in particular when the principal strains, ϵ_u, ϵ_v, are of the same sign, the actually numerically greatest shearing strain, γ_{max}, will not be given by the distance from T to the center of the circle but will be equal to either $|\epsilon_u|$ or $|\epsilon_v|$, whichever is the larger, and will occur in directions at 45° to the plane being considered.

In practice it is convenient to take the direction of one of the given gage lines as that of the axis of x.

Strains on more than three gage lines.—If strains are measured on more than three gage lines through a point, the method just discussed may still be used; but now the circle will be overdetermined, since it

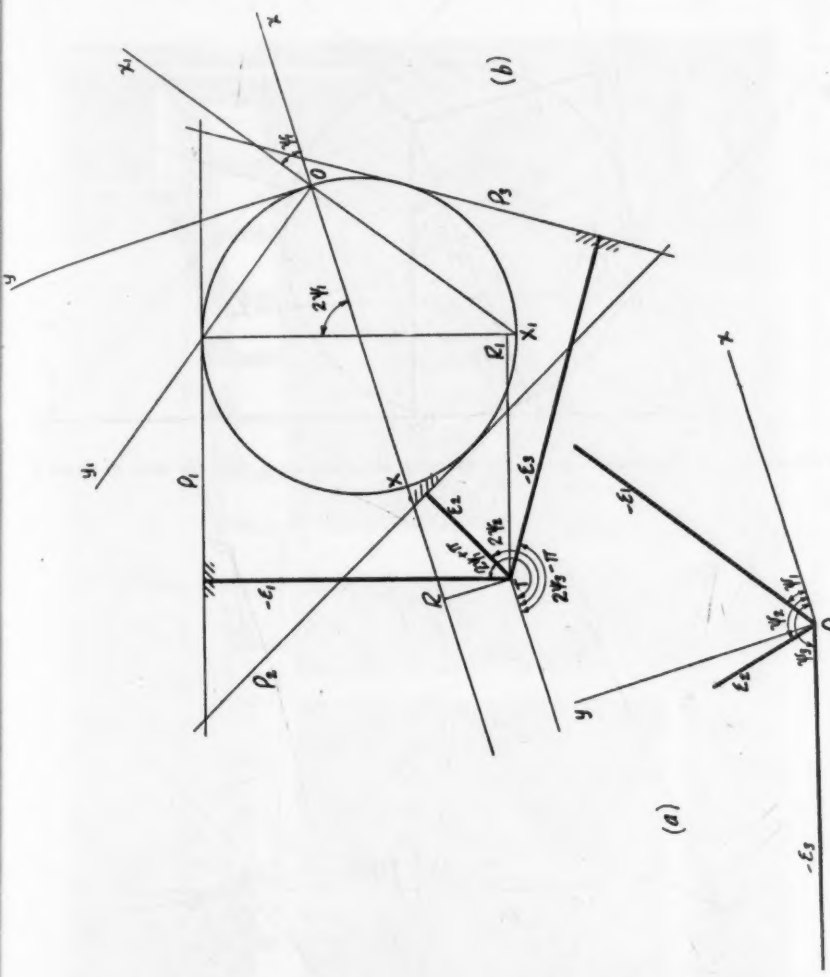


FIGURE 2.—*One positive strain and two negative strains and the corresponding circle of strain.*

must be tangent to more than three lines. The procedure is to construct, as before, the perpendiculars P_1, P_2, . . . P_n, where n is the number of gage lines on which readings are taken, and then draw the circle in such a way as to make it as nearly as possible tangent to all the lines P_1, P_2, . . . P_n.

When the principal strains and the numerically greatest shearing strain have been found, the principal stresses and the greatest shearing

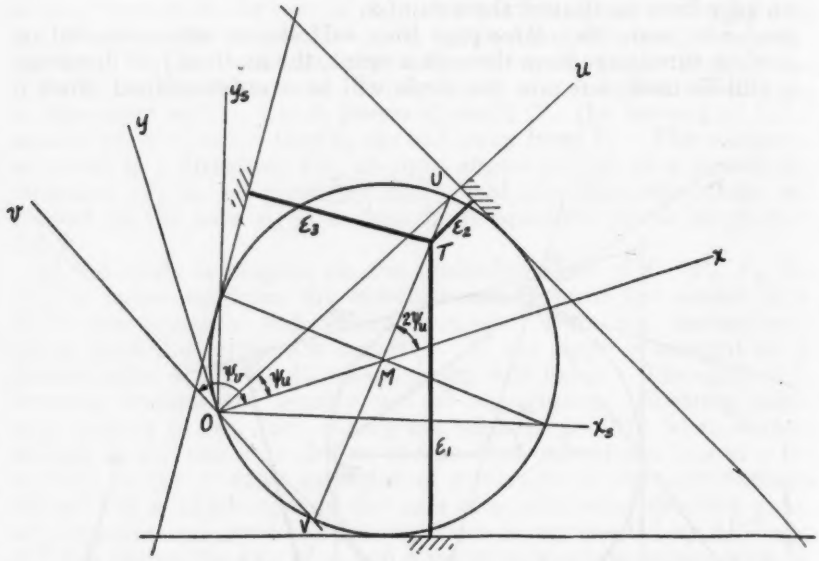


FIGURE 3.—*Principal strains and maximum shearing strain for the case of figure 1.*

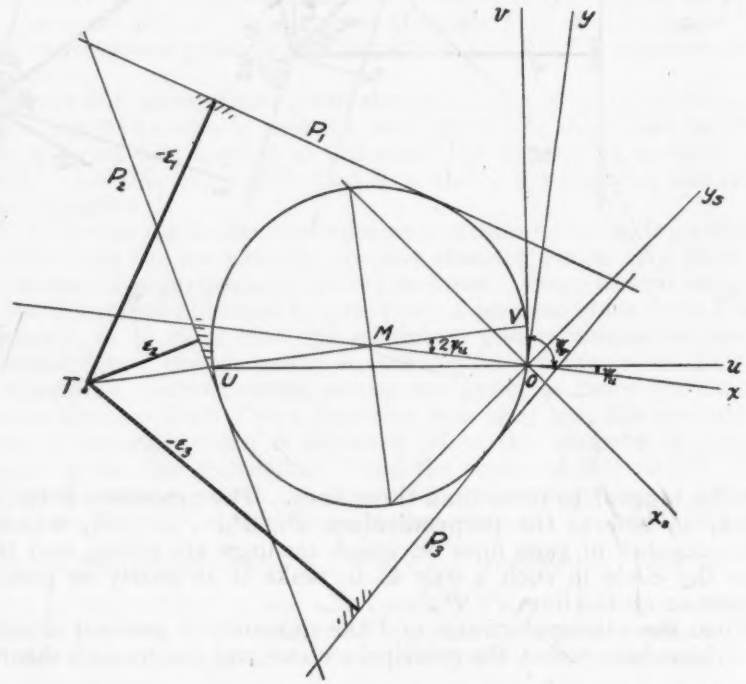
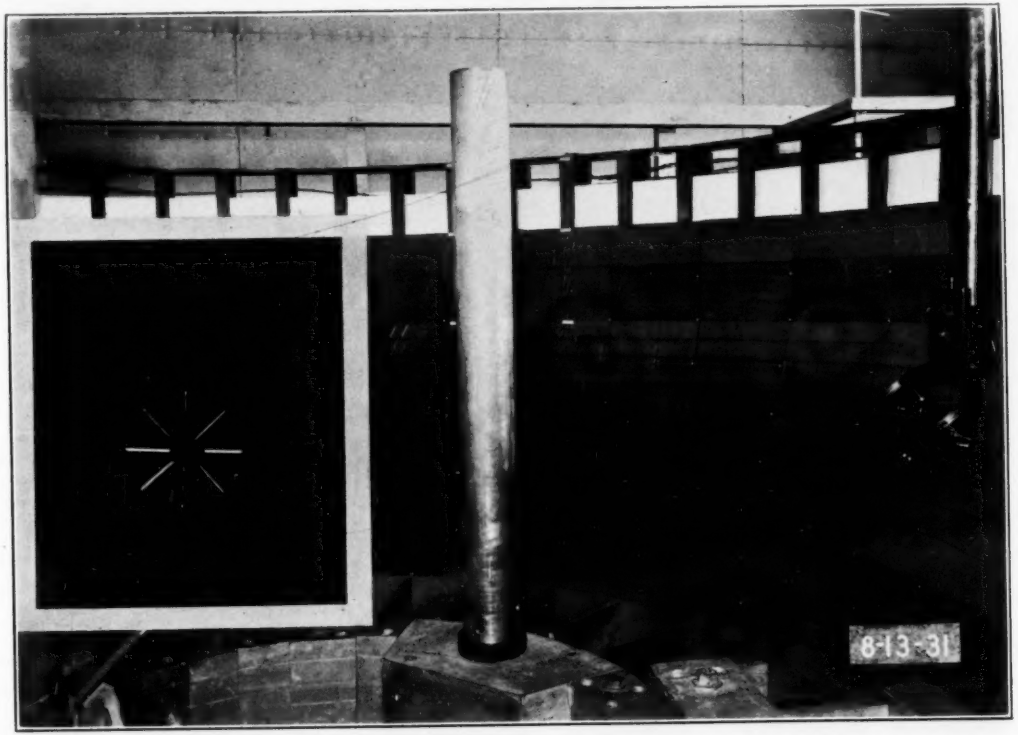


FIGURE 4.—*Principal strains and maximum shearing strain for the case of figure 2.*



UNIV. OF CALIF.

FIGURE 5.—*Downstream face of the model of Calderwood Dam showing the microscope for measuring strains and a rosette in insert.*

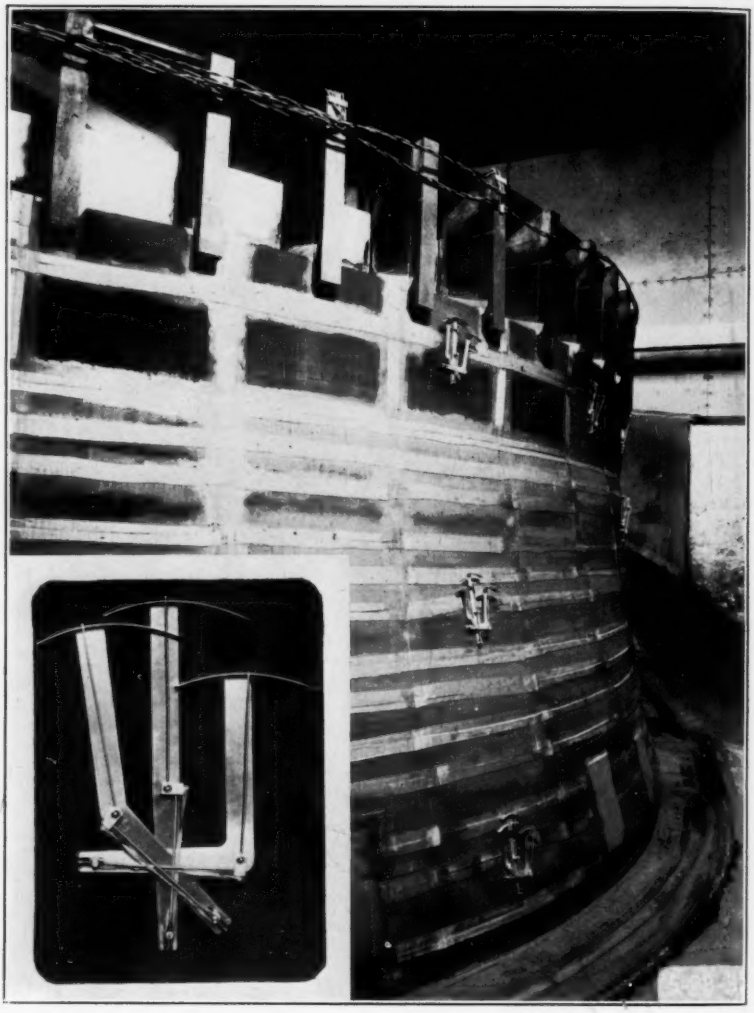


FIGURE 6.—*Upstream face of the model of Calderwood Dam showing locations of rosettes of three gage lines and the strain-measuring device used, in insert.*

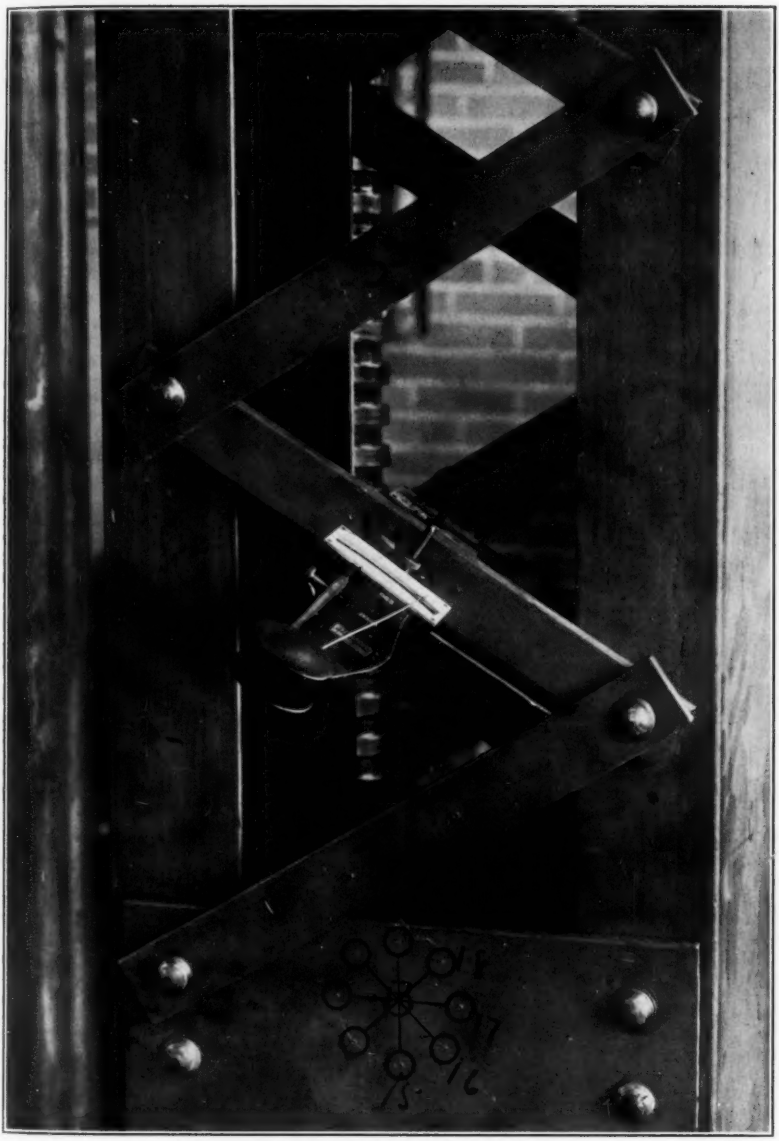


FIGURE 7.—*Built-up aluminum alloy column showing a typical rosette in the end batten plate.*

UNIV. OF MICH.

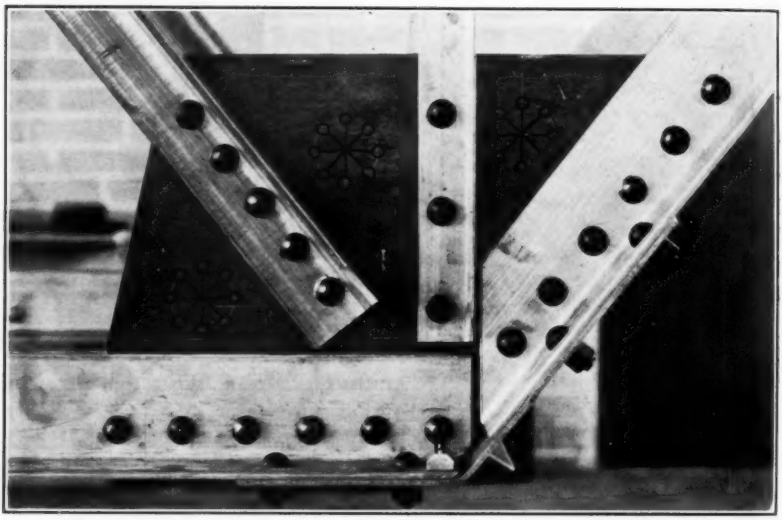


FIGURE 9.—*Gusset plate in all-aluminum truss showing rosettes of four 2-inch gage lines.*

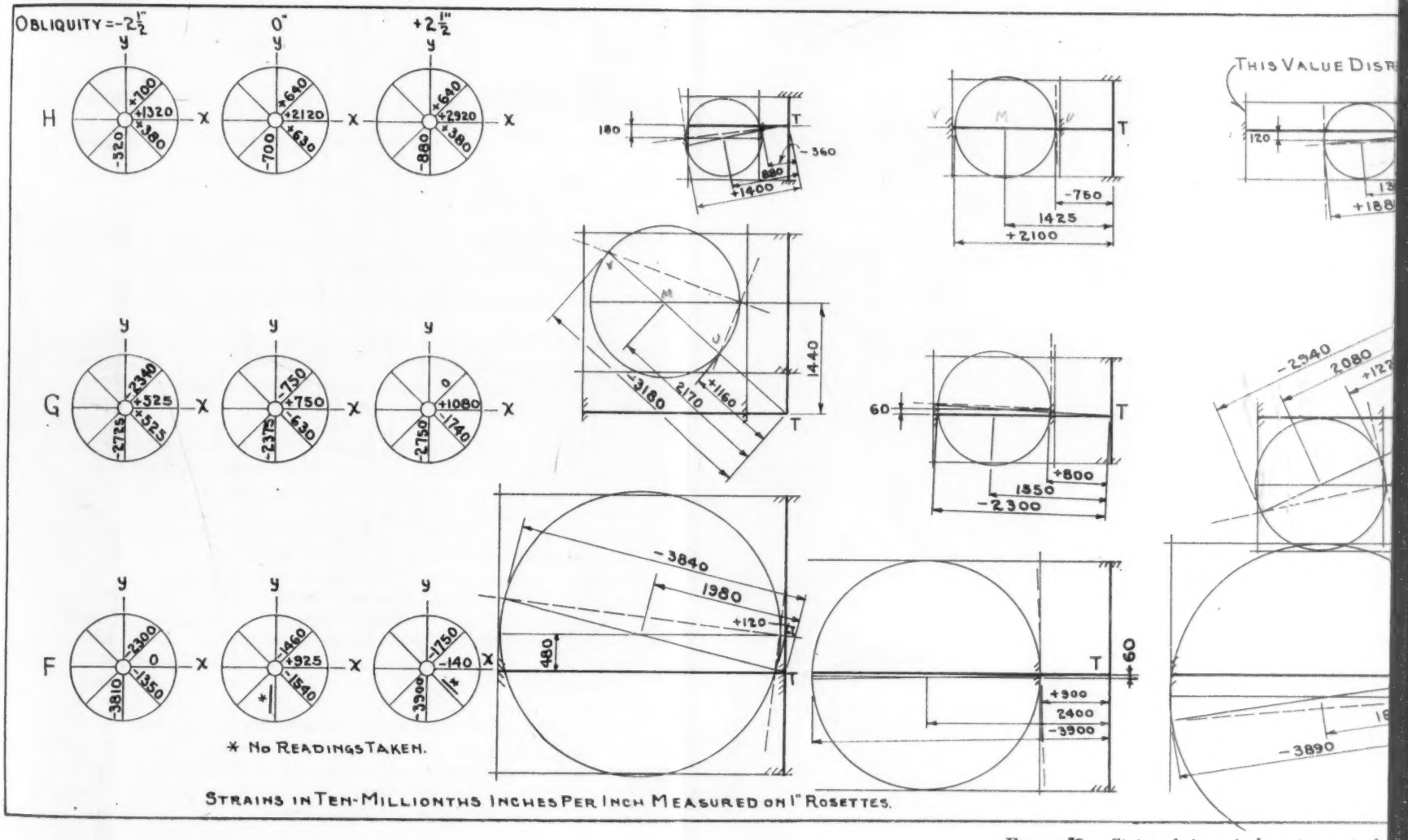
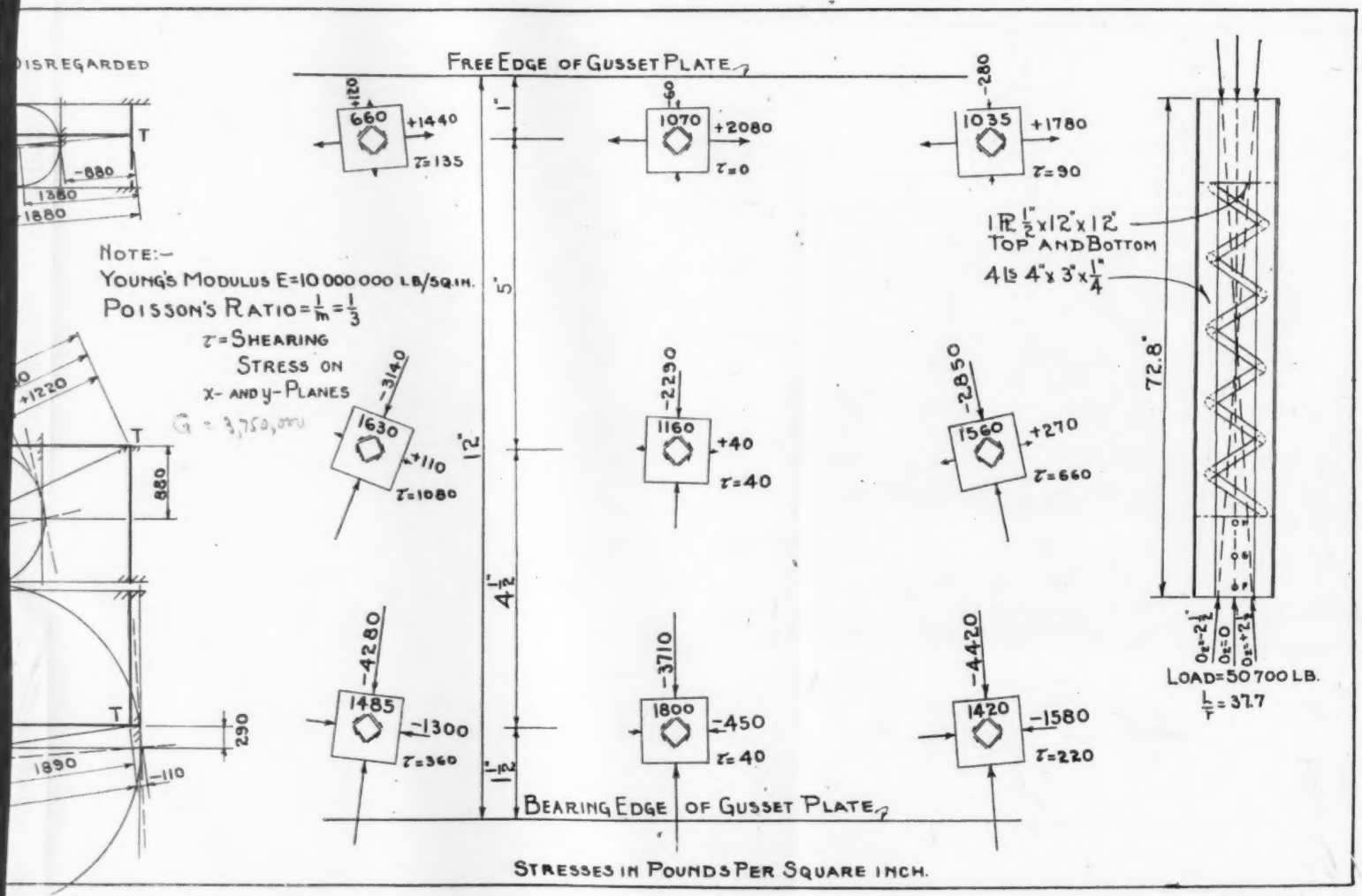


FIGURE 18.—*States of stress in lowest gusset pla*



t plates of a built-up column.

167156—33. (Face p. 690.)

stress may be determined in an elastic body from the well-known relations

$$\sigma_u = \frac{m^2 E}{m^2 - 1}\left(\epsilon_u + \frac{1}{m}\epsilon_v\right) \tag{4}$$

$$\sigma_v = \frac{m^2 E}{m^2 - 1}\left(\epsilon_v + \frac{1}{m}\epsilon_u\right) \tag{5}$$

$$\tau_{max} = G\gamma_{max}, \left(G = \frac{mE}{2(m+1)}\right) \tag{6}$$

where

σ_u and σ_v are the principal stresses in the directions u and v, respectively,

τ_{max} is the greatest shearing stress,

$\frac{1}{m}$ is Poisson's ratio,

and

E and G are the modulus of elasticity and the shearing modulus of elasticity of the material, respectively.

II. APPLICATION TO ACTUAL TESTS

The graphical method just described has been applied to numerous cases of measurements of strain in structures and structural elements, such as dams, bearing plates, beams, and gusset plates, which have been tested in the past three or four years by the Aluminum Research Laboratories.

Tests of Calderwood Dam involved measurements of strain at 42 stations on the downstream face and at three stations on the upstream face. Each station on the downstream face consisted of four intersecting 10-inch gage lines 45° apart. The particular advantage of obtaining measurements of strain on sets of intersecting gage lines, or rosettes, on such a structure is the fact that the magnitude and the direction of the principal stresses may be found, thereby indicating the general direction which the thrust on the surface of the dam takes in reaching the foundation and abutments of the dam. Besides the principal stress the horizontal, vertical, or any inclined tensions and compressions as well as the shears in the surface of the dam are given by the strains on three or more gage lines. This information is extremely valuable in studying models of dams made of an elastic material. Strain measurements on four gage lines which are not consistent among themselves may be eliminated from the first determination of the general trend, and later the erroneous reading of the strain gage may readily be detected from this general trend. In this way the remaining three strains may be used to determine the dyadic circle for that point.

Strains were measured on rosettes of three and four gage lines on both the upstream and downstream face of a rubber-compound model of Calderwood Dam [7] built and tested at the Aluminum Research Laboratories at New Kensington, Pa. Figure 5 is a general view of the downstream face of the model showing in the insert one of the

[7] A. V. Karpov and R. L. Templin, Building and Testing an Arch Dam Model, Civil Engineering, January 1932.

four gage-line rosettes which were used. Changes in gage length were measured with the filar microscope shown in the photograph. Figure 6 shows the type of three gage-line rosette used on the upstream face of the model. With strains measured on these rosettes dyadic circles were constructed from which the principal stresses and maximum shears were obtained.

The stresses in the webs of I-beams carrying concentrated loads in the case of either long, thin-webbed beams or heavier beams on short spans may be complicated by local stresses as well as by the primary shearing stresses. Measurements of strain on rosettes of three and four gage lines on the webs of aluminum-alloy I-beams and plate girders under concentrated loads have yielded direct information concerning these stresses by means of the application of the principles heretofore described.

The use of measurements of strain on rosettes for the determination of the shear in end batten plates of built-up columns under eccentric and oblique loads has proved to be very satisfactory. Figure 7 shows a typical rosette on a built-up aluminum-alloy column ready to be tested. From the results of these measurements of strain the general character of the distribution of shear in the plate was determined. Figure 8 shows the measured strains, the corresponding dyadic circles, and the principal stresses obtained for the particular cases of loading indicated.

One of the most interesting applications of measurements of strain on rosettes is that of finding the stresses in gusset plates where several members are riveted to a single plate. Figure 9 shows rosettes located on a gusset in an aluminum-alloy truss, tested to determine the transmission of stresses through gusset plates and riveted connections.

An instance of the employment of rosettes of short gage lengths (one-half inch) may be cited to demonstrate another field of application of these principles. The stresses occurring in the front end of an aluminum-alloy locomotive side rod were determined both in magnitude and direction by the use of rosettes strategically placed on the side near the end of the rod. The use of four gage lines shows the limits of accuracy of measurement by the differences in the radii of the four dyadic circles drawn from the various combinations of strains on any three of the four lines.

The examples given illustrate the wide range of cases to which such measurements of strain may be applied. It is only through some such measurements that a complete picture of the state of stress in a body of two principal dimensions or in the surface of a body of three dimensions can be obtained.

WASHINGTON, February 14, 1933.

CRITICAL SOLUTION TEMPERATURES OF MIXTURES OF GASOLINE, ETHYL ALCOHOL, AND WATER

By Oscar C. Bridgeman and Dale Querfeld

ABSTRACT

One of the major difficulties encountered with the use of ethyl alcohol-gasoline mixtures as motor fuels arises from the limited solubility of ethyl alcohol in gasoline. Data are presented on the critical solution temperatures of mixtures of eight different gasolines, in proportions from 10 to 90 percent gasoline, with each of eight alcohol solutions containing from 1 to 8 percent of water by volume. It was found that the critical solution temperature decreased markedly as the concentration of water in the alcohol solution decreased and as the percentage of gasoline in the mixture decreased. The critical solution temperatures were found to differ considerably with various gasolines. The present work indicates that addition of other substances to increase the solubility of the alcohol is necessary if gasoline-alcohol mixtures that will not separate in service are to be obtained, unless alcohol almost entirely free from water is employed. The data obtained show that mixtures of gasoline and 95 percent alcohol in equal proportions separate into two phases at temperatures ranging from 14° to 41° C., for the eight gasolines studied. If 95 percent alcohol is employed, the alcohol content of the mixture must be not less than about 90 percent, in order that the separation temperature may be below −20° C. On the other hand, if 99 percent alcohol is employed, the alcohol content of the mixture can be as low as 10 percent, without separation down to −20° C.

CONTENTS

		Page
I.	Introduction	693
II.	Experimental apparatus and procedure	694
III.	Concentration of alcohol-water solutions employed	697
IV.	Experimental data	698
V.	Discussion of experimental data and conclusions	703

I. INTRODUCTION

Interest in the possibility of using mixtures of gasoline and ethyl alcohol as motor fuels began almost with the advent of the automobile. This interest has arisen largely from the desire to conserve natural petroleum resources, to provide an outlet for excess production of ethyl alcohol, or to furnish a market for agricultural products by transforming them into ethyl alcohol.

One of the major technical difficulties which has been encountered arises from the limited solubility of ethyl alcohol in gasoline, unless the ethyl alcohol is almost free from water. This is particularly serious in climates in which freezing temperatures occur during the winter. Furthermore, provision must be made for the possibility of absorption of moisture during use, which makes it essential to introduce a suitable factor of safety as a precautionary measure. Due to the low solubility of commercial (95 percent) ethyl alcohol in gasolines, particularly at low temperatures, it is necessary either to use alcohol

almost free from water or to add other substances to increase the solubility. Preparatory to an investigation of such substances, it seemed desirable to obtain a comprehensive set of data on the solubility in a number of gasolines of ethyl alcohol containing various percentages of water. The present paper covers the information obtained in this preliminary investigation, using eight different gasolines, and includes data obtained on the temperatures below which ethyl alcohol containing up to 8 percent of water is not completely miscible with each of these gasolines when blended in various proportions from 10 to 90 percent of gasoline.

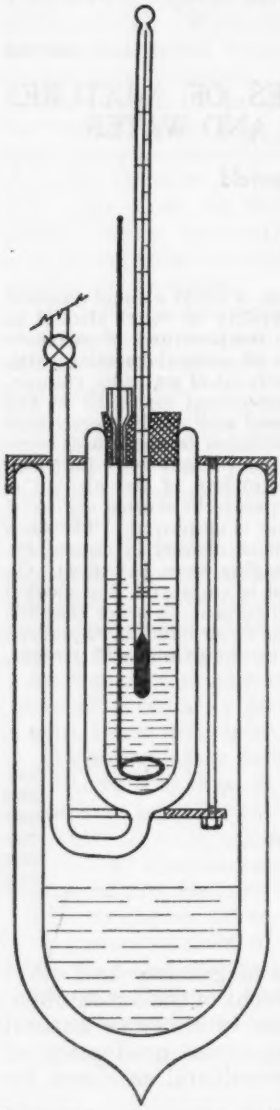


FIGURE 1.—*Apparatus used for the measurement of the critical solution temperatures of gasoline-alcohol mixtures.*

There appears to be little published information on the subject. A number of investigators [1] have used the solubility in kerosene as a criterion of the water content of ethyl alcohol and have given some data on critical solution temperatures for alcohol containing various percentages of water. A limited set of data on the solubility of aqueous ethyl alcohol solutions in six gasolines has been given by Ormandy and Craven.[2] Hubendick [3] also gives a few values for the solubility of alcohol in motor gasoline. Nicolardot [4] has done considerable work on the solubility problem when aromatic hydrocarbons or other materials are added, but did little work on simple blends of ethyl alcohol and gasoline. Data on one aviation gasoline have also been reported by Sparrow.[5]

II. EXPERIMENTAL APPARATUS AND PROCEDURE

The general procedure used in the present work consisted in preparing quantitatively solutions of ethyl alcohol, of known water content, and gasoline, and in measuring the critical solution temperatures by noting the appearance of a second phase on cooling.

A diagram of the apparatus used for measuring the critical solution temperatures is shown in figure 1. The tube used for holding the alcohol-gasoline blend during the determination was similar to a Dewar cylinder except that a glass tube was connected to the bottom so as to permit varying the air pressure in the annular space in order

[1] For a complete discussion of work along these lines together with references, see McKelvy, B.S.Bull. vol. 9, p. 344, 1913.
[2] Ormandy and Craven, Proc. Inst. Auto. Eng., vol. 18 (1), p. 313, 1924.
[3] Hubendick, Trans. Fuel Conference. World Power Conference, vol. 3, p. 724, 1928.
[4] Nicolardot, La Technique Automobile, No. 115, fourth Trimestre, 1921.
[5] Sparrow, N.A.C.A. Technical Report, No. 232, 1925.

to control the rate of heat transfer across this space. The inside tube of the double-walled container was 20 mm in diameter and 150 mm long, and the width of the annular space was 2 mm. A cork stopper was used to close tightly the mouth of the tube and provision was made for inserting a thermometer and a stirrer. The thermometer was supported by making it fit tightly in the cork stopper. The stirrer was made of ⅛-inch brass rod, bent into a loop at the bottom. A packing gland was employed where the stirrer rod passed through the cork stopper. This gland consisted simply of a brass tube, of design shown in figure 1, which fitted tightly into a hole in the cork stopper, and the space between the brass tube and the rod passing through it was filled with absorbent cotton. A packing gland was found to be necessary to prevent absorption of moisture by the alcohol-gasoline mixture. A special brass holder, shown in figure 1, was constructed for holding the double-walled container. A Dewar cylinder was provided for holding the liquid used to cool the alcohol-gasoline mixture.

A mercury-in-glass thermometer graduated in 0.2° C. was used for temperature measurements down to −36° C., while for temperatures below this, a toluene thermometer similarly graduated was employed. Both thermometers were calibrated as partial immersion instruments.

Immediately before each determination, the particular alcohol-gasoline mixture under investigation was prepared. By means of calibrated pipettes, appropriate amounts of the alcohol and gasoline were introduced into a small ground-stoppered flask, where they were thoroughly mixed and warmed if necessary in order to effect solution. No special precautions were taken to prepare the mixtures at any definite temperature, since the coefficients of expansion of the gasolines and the aqueous alcohol solutions were so nearly alike, being on the average 0.00115 for the former and 0.00108 for the latter. If the gasoline and the alcohol solution were at the same temperature when mixed, then a variation in mixing temperature of 20° C., which was a maximum for the present work, would introduce an error in the amount of each constituent in the mixture of less than 2 parts in 1,000, when referred to 60° F. as the standard temperature. Precautions were taken, however, to insure that the gasoline and the ethyl alcohol solution were very close to the same temperature before mixing, by storing their respective containers in close proximity to one another. A temperature difference of 2° C. would introduce an error in the amount of each constituent in the mixture of only 2 parts in 1,000. While greater precision could have been obtained by preparing the mixtures at a definite temperature, the general accuracy desired did not appear to warrant the more elaborate procedure necessary for high precision.

About 15 ml of the mixture was transferred to the double-walled container, which was then closed with the stopper holding the thermometer and stirrer. In order to prevent separation of the alcohol-gasoline mixture into two phases during this transfer, the double-walled container was warmed if necessary. In the above procedure of preparing the mixtures and transferring them to the apparatus preparatory to making a measurement, the pipettes, the flask, the double-walled container, the thermometer, and the stirrer were all carefully cleaned and dried in advance.

After the introduction of the sample, the tube was placed in the brass holder and was inserted into the Dewar cylinder containing either liquid air or cold water, depending upon the anticipated critical

solution temperature. The rate of cooling was maintained at 1° to 2° C. per minute, either by controlling the pressure in the air space between the double walls of the container, or by regulating the depth of immersion in the cooling medium, or by adjusting the height of cooling liquid in the Dewar cylinder. All three methods were employed, although a combination of the last two was found to be the most convenient. In general, the temperature of the sample was adjusted to a value about 5° to 10° C. above the anticipated critical solution temperature before each determination. As the temperature dropped, the mixture was stirred vigorously until at some definite temperature for each mixture, a turbidity suddenly appeared, indicating the separation of a second phase. This temperature was recorded as the critical solution temperature, being the lowest temperature at which the alcohol solution and gasoline under investigation are completely miscible in the given proportions employed. A check deter-

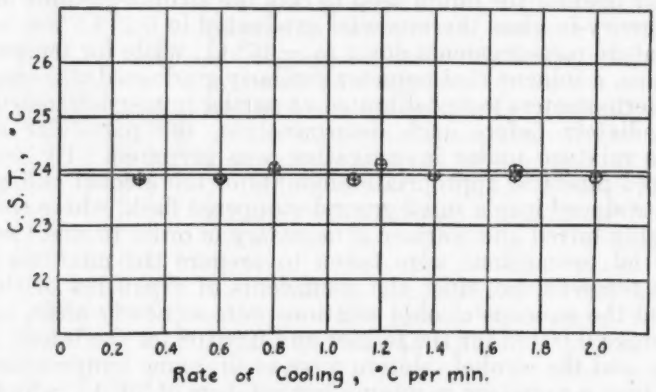


FIGURE 2.—*Data on the critical solution temperature (C.S.T.) of a representative mixture measured at different rates of cooling*

mination was made on each mixture without removing the sample in order to determine whether there was any significant rate of absorption of moisture during the measurement. Duplicate values agreed very well, the average difference being less than 0.2° C. In a number of cases, the temperatures were read at which the turbidity disappeared on heating. These values checked the temperatures at which turbidity appeared on cooling, within 0.2° C. on the average, thus assuring that the critical solution temperatures measured were very close to the equilibrium values.

The rate of cooling employed, namely, 1° to 2° C. per minute, was chosen on the basis of preliminary experiments made to establish a rate of cooling which would expedite the measurements and still permit the attainment of the desired accuracy. A representative set of data are shown in figure 2. It is seen that there is no trend in the values of the measured critical solution temperature over the range of rates of cooling investigated.

III. CONCENTRATION OF ALCOHOL-WATER SOLUTIONS EMPLOYED

Eight ethyl alcohol solutions were used containing volume percentages of alcohol ranging from about 93 to 99 percent. These solutions were prepared from pure, absolute ethyl alcohol by addition of appropriate amounts of distilled water, and shaking thoroughly. The composition of the alcohol-water solutions was determined from measurements of their density. The pycnometers used had approximate volumes of 21 ml and were of the type described by Osborne.[6] They were carefully calibrated with distilled water at 30.00° C. which was the temperature used in all density measurements. Check determinations were made on all alcohol solutions, the precision in measurement being 1 part in 5,000.

The alcohol solutions were made up in batches of 1 liter at a time and were stored in flasks with ground stoppers. New solutions of approximately the same concentrations were prepared when needed. The concentration of each alcohol solution was checked periodically, and the solution was discarded if the volume percent of alcohol changed by more than 1 part in 2,000. In most cases, the solution was used up before a change of this magnitude was observed.

The average compositions of the various ethyl alcohol solutions employed are given in table 1, where letters are used to designate solutions differing in concentration by about 0.8 volume percent of alcohol, while numbers are used to designate successive batches of solutions of the same approximate composition. Values of the 60°/60° specific gravity, and of the 60° F. volume percentages of ethyl alcohol and of water are given. Volume percent is the volume of pure ethyl alcohol, or of pure water, respectively, at 60° F. in 100 ml of solution at 60° F. Since there is a contraction in volume on mixing ethyl alcohol and water, the sum of the volume percentages of these two constituents exceeds 100.

TABLE 1.—*Concentrations of ethyl-alcohol solutions*

No.	60°/60° specific gravity	Volume percent alcohol at 60° F.	Volume percent water at 60° F.
A	0.79820	99.144	1.110
A1	.79826	99.131	1.127
B	.80202	98.337	2.133
B1	.80207	98.325	2.149
B2	.80199	98.344	2.124
C	.80565	97.528	3.130
C1	.80580	97.492	3.182
C2	.80586	97.479	3.199
D	.80917	96.703	4.145
D1	.80927	96.679	4.175
D2	.80930	96.672	4.184
E	.81269	95.845	5.178
E1	.81274	95.833	5.193
E2	.81257	95.875	5.143
F	.81608	94.987	6.196
F1	.81609	94.984	6.201
F2	.81615	94.970	6.218
G	.81948	94.097	7.243
G1	.81940	94.119	7.217
G2	.81961	94.061	7.285
H	.82264	93.243	8.237
H1	.82281	93.196	8.291
H2	.82275	93.210	8.275

[6] Osborne, B.S.Bull, vol. 9, p. 405, 1913.

IV. EXPERIMENTAL DATA

Data were obtained on eight motor gasolines which are described in table 2. The first six fuels were straight-run products, obtained from a number of different crude oils. The last two fuels were 100 percent cracked products, obtained by two different cracking processes.

With each gasoline, mixtures containing from 10 to 90 percent gasoline by even steps of 10 percent were prepared with the alcohol solution of each concentration, and measurements of the critical solution temperature were made. There was no attempt to measure critical solution temperatures lying outside of the approximate range from +65° to −65° C. No account was taken of any change in volume on mixing the gasoline with the alcohol solution. Accordingly, the volume percent of gasoline in the mixture, referred to throughout this paper is the volume of gasoline at 60° F. which, when mixed with the appropriate volume of alcohol solution, gives a summation of volumes equal to 100 at 60° F. It is considered that the volume percents of gasoline were accurate to better than 0.5 units.

TABLE 2.—*Identification data on gasolines*

No.	Source	Temperature at stated percentages evaporated			60°/60° specific gravity
		10 percent	50 percent	90 percent	
		°C.	°C.	°C.	
1	Pennsylvania	76	135	199	0.738
2	Rumania	70	106	152	.734
3	California	66	108	154	.730
4	Oklahoma	72	124	194	.740
5	California	58	110	156	.732
6	East Texas	58	110	162	.723
7	100 percent cracked	54	126	188	.754
8	do	69	142	194	.773

The data obtained on the eight gasolines are given in tables 3 to 10, inclusive. The critical solution temperatures recorded are the means of two determinations on each mixture. It is seen that the critical solution temperature decreases markedly as the concentration of the water in the alcohol solution decreases and as the percentage of gasoline in the mixture decreases.

The values for gasolines nos. 1 and 7 are shown graphically in figures 3 and 4, where the different curves correspond to the data on the blends with the various alcohol solutions. These two gasolines were chosen for illustration, since the critical solution temperatures for the former are the highest obtained for the gasolines investigated, while the critical solution temperatures for the latter are the lowest values obtained. The data on these two gasolines are plotted in a different manner in figures 5 and 6 to show the critical solution temperatures for various percentages of water in the mixtures. In this case the different curves correspond to various percentages of gasoline in the mixtures.

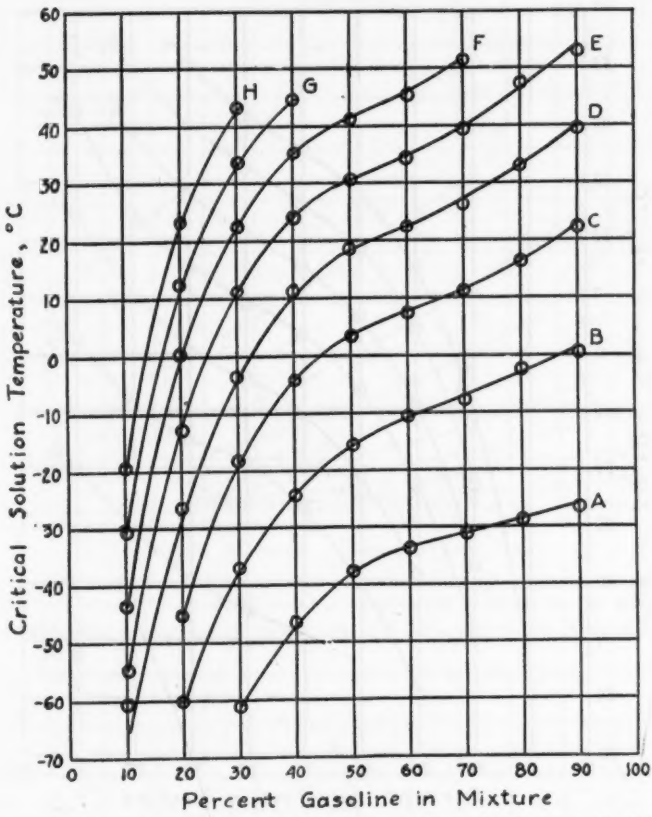


FIGURE 3.—*Data on the critical solution temperatures of mixtures of ethyl alcohol and gasoline no. 1 in various proportions.*

Each curve represents values on mixtures with ethyl alcohol of a definite alcohol concentration symbolized by a letter and recorded in table 1.

TABLE 3.—*Critical solution temperatures of mixtures with gasoline no. 1*

Alcohol solution	Volume percent gasoline in mixture								
	10	20	30	40	50	60	70	80	90
	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.
A			−61.0	−46.2	−37.4	−33.4	−31.0	−28.3	−26.4
B		−60.0	−36.8	−24.0	−15.1	−10.3	−7.4	−2.5	.8
C		−45.0	−18.0	−4.1	3.7	7.7	11.3	16.6	22.3
D	−60.6	−26.2	−3.2	11.5	18.7	22.4	26.6	33.1	39.4
E	−54.7	−12.7	11.3	24.3	30.8	34.4	39.5	47.7	52.9
F	−43.2	.3	22.5	35.3	41.6	45.7	51.6		
G	−30.2	12.6	33.7	45.0					
H	−19.3	23.2	43.2						

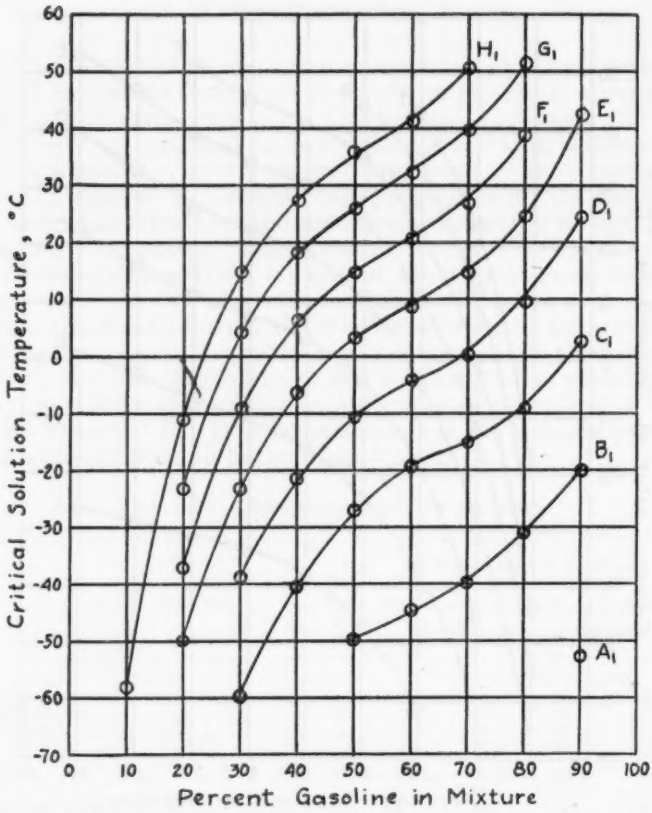


FIGURE 4.—*Data on the critical solution temperatures of mixtures of ethyl alcohol and gasoline no. 7 in various proportions.*

Each curve represents values on mixtures with ethyl alcohol of a definite alcohol concentration symbolized by a letter and recorded in table 1.

TABLE 4.—*Critical solution temperatures of mixtures with gasoline no. 2*

Alcohol solution	Volume percent gasoline in mixture								
	10	20	30	40	50	60	70	80	90
	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.
A					−67.0	−60.7	−55.6	−52.3	−47.9
B				−56.5	−43.6	−35.3	−30.4	−24.2	−16.2
C			−53.5	−34.5	−21.5	−15.0	−10.8	−3.0	7.6
D		−59.9	−35.4	−16.5	−5.4	−0.2	5.8	14.5	27.0
E		−47.9	−18.5	−1.3	8.5	14.0	19.7	29.4	41.9
F		−33.2	−1.5	11.1	20.1	25.6	32.4	44.4	
G		−20.4	7.3	22.2	30.7	36.5	44.4		
H	−57.0	−7.8	17.7	32.2	40.7	46.4			

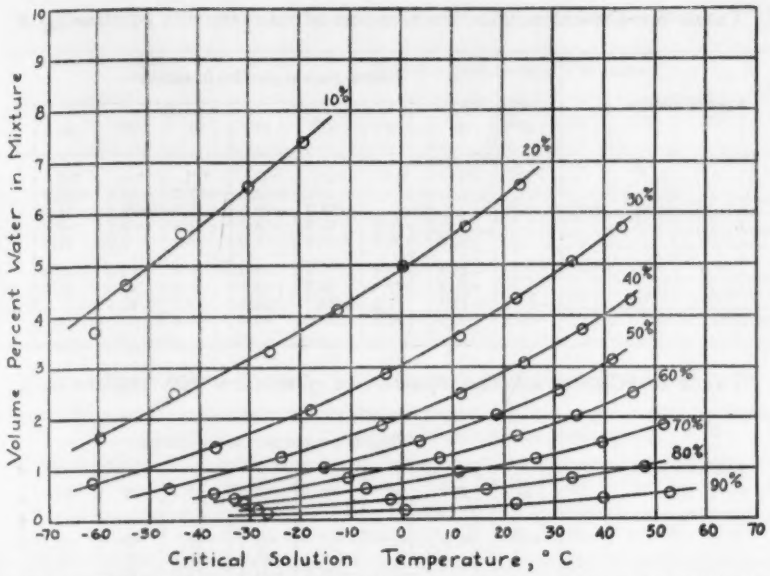


FIGURE 5.—*Data on the critical solution temperatures of mixtures of ethyl alcohol and gasoline no. 1 for various volume percentages of water in the mixtures.*

The different curves represent different constant percentages of gasoline in the mixtures.

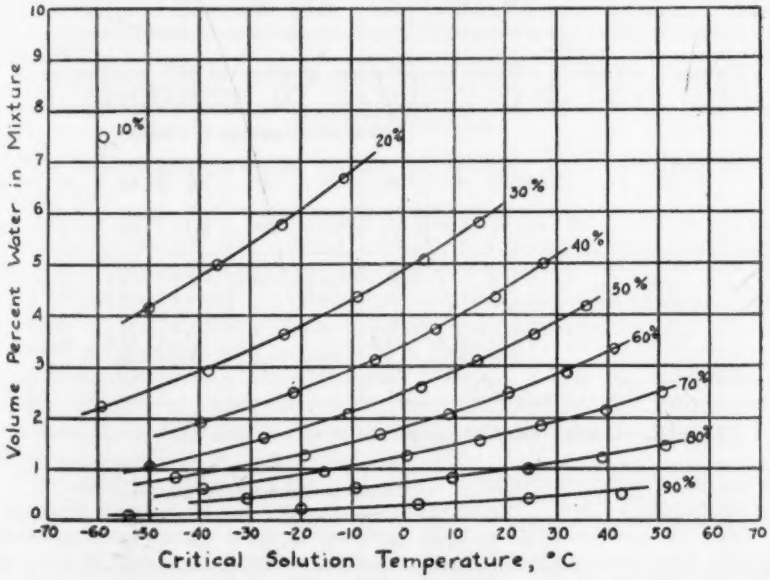


FIGURE 6.—*Data on the critical solution temperatures of mixtures of ethyl alcohol and gasoline no. 7 for various volume percentages of water in the mixtures.*

The different curves represent different constant percentages of gasoline in the mixtures.

167156—33——9

TABLE 5.—*Critical solution temperatures of mixtures with gasoline no. 3*

Alcohol solution	Volume percent gasoline in mixture—								
	10	20	30	40	50	60	70	80	90
	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.
A					−64.8	−57.7	−54.5	−50.0	−44.3
B				−52.3	−40.6	−33.8	−28.2	−21.4	−12.5
C			−46.3	−31.2	−19.7	−12.8	−7.2	−0.2	10.2
D		−60.4	−28.3	−13.0	−3.0	3.4	9.3	17.1	29.7
E		−45.3	−11.6	1.6	10.9	16.8	22.6	32.2	43.6
F		−31.8	−2.8	13.4	22.5	28.0	35.3	46.7	
G	−65.0	−17.4	11.3	24.7	33.5	39.1	47.0		
H	−54.9	−6.2	21.1	35.0	44.0	49.3			

TABLE 6.—*Critical solution temperatures of mixtures with gasoline no. 4*

Alcohol solution	Volume percent gasoline in mixture—								
	10	20	30	40	50	60	70	80	90
	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.
A1					−51.2	−45.4	−41.1	−34.2	−29.3
B1			−51.1	−33.5	−24.4	−18.2	−12.9	−7.9	−1.4
C1		−54.1	−31.1	−14.3	−5.2	1.6	5.0	11.3	19.5
D1		−41.3	−13.5	1.3	9.5	14.6	19.4	27.6	37.5
E1		−25.0	0.0	15.0	22.0	26.8	32.2	41.3	53.3
F1	−55.2	−11.3	12.3	26.2	33.8	37.7	44.6		
G1	−44.3	1.0	24.6	36.9	44.2	48.2			
H1	−31.7	12.0	34.1	46.0	52.3				

TABLE 7.—*Critical solution temperatures of mixtures with gasoline no. 5*

Alcohol solution	Volume percent gasoline in mixture—								
	10	20	30	40	50	60	70	80	90
	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.
A1								−50.4	−43.2
B1					−42.5	−34.0	−28.5	−22.0	−11.8
C1			−52.1	−34.4	−20.4	−14.2	−8.5	−.3	12.5
D1			−35.6	−15.8	−4.1	2.8	8.4	17.7	31.1
E1		−49.1	−18.8	−0.9	9.7	15.5	22.2	32.4	46.2
F1		−33.7	−5.0	12.1	20.5	27.4	34.6	46.4	
G1		−20.3	7.4	23.2	32.1	37.9	46.1		
H1		−8.5	18.4	33.1	41.7	47.7			

TABLE 8.—*Critical solution temperatures of mixtures with gasoline no. 6*

Alcohol solution	Volume percent gasoline in mixture—								
	10	20	30	40	50	60	70	80	90
	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.
A1								−46.0	−39.8
B2				−48.3	−37.9	−29.4	−25.1	−19.5	−10.2
C2			−47.9	−28.2	−16.6	−9.6	−4.5	2.2	13.7
D2		−59.2	−29.3	−11.4	−.4	5.7	10.8	19.7	33.0
E2		−43.0	−13.9	3.2	13.4	18.7	24.7	35.0	46.0
F2		−26.5	0.0	15.7	24.2	30.0	37.1	49.7	
G2		−14.4	12.5	26.8	36.0	41.0	49.3		
H2	−50.9	−2.1	23.0	36.6	44.4	50.0			

TABLE 9.—*Critical solution temperatures of mixtures with gasoline no. 7*

Alcohol solution	Volume percent gasoline in mixture—								
	10	20	30	40	50	60	70	80	90
	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.
A1									−53.1
B1					−49.8	−44.8	−40.1	−30.9	−19.9
C1			−59.9	−40.0	−26.8	−19.3	−15.9	−9.3	2.8
D1			−38.8	−21.6	−10.9	−4.6	.7	9.6	24.5
E1		−50.2	−23.7	−6.5	3.5	8.6	14.8	24.4	42.6
F1		−37.0	−9.1	6.2	14.7	20.2	27.0	39.0	
G1		−23.6	4.0	18.0	25.8	32.0	39.4	51.4	
H1	−58.1	−11.6	14.5	27.4	35.5	41.1	50.5		

TABLE 10.—*Critical solution temperatures of mixtures with gasoline no. 8*

Alcohol solution	Volume percent gasoline in mixture—								
	10	20	30	40	50	60	70	80	90
	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.
A1								−51.7	−45.6
B1					−50.9	−40.9	−34.9	−28.2	−22.7	−13.9
C1			−48.8	−30.0	−18.5	−13.3	−9.2	−.8	9.8
D1		−56.8	−28.2	−12.0	−1.5	2.1	8.2	15.9	27.4
E1		[1] −42.3	[1] −14.1	1.9	11.2	15.5	21.9	31.5	45.9
F1		−27.2	−.7	14.1	21.8	26.6	33.3	44.3	
G1		−13.6	13.3	25.4	33.1	37.6	45.8		
H1	−49.8	−2.0	22.0	34.6	41.8				

[1] Solution E2.

V. DISCUSSION OF EXPERIMENTAL DATA AND CONCLUSIONS

The experimental data herein presented lead to three general conclusions:

1. With any given percentage of gasoline in the mixture between 10 and 90 percent, the critical solution temperature rises as the percentage of water in the ethyl alcohol increases.

2. With any given ethyl alcohol solution, containing from 1 to 8 percent of water, the critical solution temperature rises as the percentage of gasoline in the mixture is increased.

3. With any given percentage of gasoline in the mixture between 10 and 90 percent, and with any given ethyl alcohol solution containing from 1 to 8 percent of water, the critical solution temperatures differ considerably with various gasolines.

The differences in the critical solution temperatures with various gasolines are due to differences in composition. Such differences may be associated partly with differences in volatility and partly with differences in the crude from which the gasoline was refined and the type of refining process used. Consideration of the data for the straight-run gasolines nos. 2 and 3, which have about the same volatility, shows that the critical solution temperatures for these two gasolines do not differ much, even though they are refined from different crude oils. A similar conclusion is reached on comparing the data for gasolines

nos. 5 and 6, which also have about the same volatility. While these conclusions are suggestive as regards the relative effects of volatility and source of crude oil, the data do not permit the quantitative evaluation of these two effects independently. In a later paper more definite information will be presented regarding the effect of variations in volatility on the critical solution temperatures.

The present data indicate definitely that separation would occur at any temperature below 0° C. with any of the gasolines investigated when mixed with less than 50 percent of ethyl alcohol, unless the alcohol contains less than 3 to 5 percent of water. Even this concentration of alcohol leaves no margin of safety for absorption of moisture from the air after mixing and while in the supply tank of the automotive vehicle. A margin of safety is particularly desirable since separation into two liquid layers occurs at a temperature immediately below that at which turbidity is noted. With provision for a margin of safety to compensate for absorption of moisture, the alcohol used would have to be almost entirely free from water in order to prevent separation even at 0° C. Since it is believed that the gasolines investigated cover the range of gasolines commercially available, it is considered that addition of other substances to increase the solubility of the alcohol is necessary if gasoline-alcohol mixtures that will not separate in service are to be obtained, unless alcohol almost entirely free from water is employed. Information on the effectiveness of added substances in increasing the solubility of alcohol in gasoline, and on the required margin of safety against absorption of moisture from the air in service, is necessary before any safe estimate can be made of the highest permissible water content of the alcohol.

WASHINGTON, March 23, 1933.

○